Phosphine-Catalyzed Enantioselective Intramolecular [3+2] Cycloadditions to Generate Fused Ring Systems

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Supporting Information

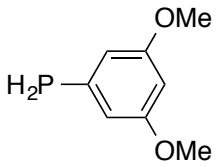
Table of Contents

I. General Information

Unless otherwise noted, all materials were purchased from commercial suppliers. Toluene, THF, and Et_2O were purified prior to use by passage through a column of neutral alumina under argon.

^{13}C NMR spectroscopic data for all phosphorus-containing compounds were collected on a Varian 600 MHz spectrometer at ambient temperature with ^{1}H and ^{31}P decoupling. HPLC analyses were carried out on an Agilent 1100 Series system with Daicel CHIRALCEL® and CHIRALPAK® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm).

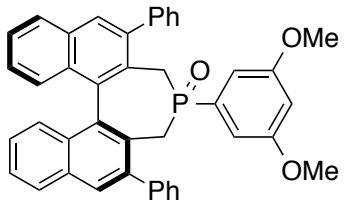
II. Preparation of Catalyst 4



(3,5-Dimethoxyphenyl)phosphane. In a nitrogen-filled glovebox, $LiAlH_4$ (376 mg, 9.90 mmol), Et_2O (anhydrous; 8.5 mL), and a stir bar were added to a 40-mL vial, and then diethyl

(3,5-dimethoxyphenyl)phosphonate[1] (904 mg, 3.30 mmol) was added dropwise. Next, the vial was capped and removed from the glovebox, and a nitrogen-filled balloon was attached to the vial. The reaction mixture was stirred at r.t. for 12 h. Then, Et_2O (5 mL) and NaOH (15% in water; 0.4 mL) were added, and the mixture was stirred for 20 min. Next, the solution was dried over $MgSO_4$, filtered, and concentrated under reduced pressure, which furnished the phosphine as a light-yellow oil (analysis by ^1H NMR spectroscopy showed some impurities). The unpurified phosphine was used in the next step without further purification (if it is stored, it should be kept under an inert atmosphere).

^1H NMR (300 MHz, $CDCl_3$) δ 8.58 (dd, 2H, *J* = 7.7 Hz, *J* = 2.4 Hz), 8.34–8.32 (m, 1H), 6.27 (m, 1H), 5.72 (s, 6H), 5.60–5.59 (m, 1H).



(11b*S*)-4-(3,5-Dimethoxyphenyl)-2,6-diphenyl-3,5-dihydrodinaphtho[2,1-*c*:1',2'-*e*]phosphepine 4-oxide. In a nitrogen-filled glovebox, (*S*)-2,2'-bis(chloromethyl)-3,3'-diphenyl-1,1'-binaphthalene[2,3] (790 mg, 1.57 mmol), THF (anhydrous; 50 mL), and a stir bar were added to a 100-mL round-bottom flask. Sodium hydride (98 mg, 4.1 mmol) and a solution of (3,5-dimethoxyphenyl)phosphane (400 mg, 2.35 mmol) in THF (10 mL) were added in turn. The flask was fitted with a rubber septum and then removed from the glovebox. A nitrogen-filled balloon was attached to the flask, which was then heated to 60 °C. After 20 h, the mixture was allowed to cool to room temperature, H_2O (3 mL) was added, and the mixture was concentrated under reduced pressure. CH_2Cl_2 (50 mL), H_2O (10 mL), and H_2O_2 (50% aqueous; 1.5 mL) were added in turn, and the mixture was stirred at r.t. for 1 h. Next, it was cooled to 0 °C, and then a solution of $Na_2S_2O_3$ (aqueous, saturated; 20 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (20 mL x 3), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (5% EtOAc in CH_2Cl_2→40% EtOAc in CH_2Cl_2), which afforded the phosphine oxide as a white crystalline solid (780 mg, 81%).

^1H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.96 (d, 1H, *J* = 7.7 Hz), 7.89 (d, 1H, *J* = 7.3 Hz), 7.77 (s, 1H), 7.50–7.44 (m, 5H), 7.38–7.34 (m, 1H), 7.29–7.21 (m, 5H), 7.19–7.18 (m, 1H), 7.15–7.14 (m, 2H), 6.85 (br s, 2H), 6.51 (t, 1H, *J* = 2.6 Hz), 6.18 (dd, 2H, *J* = 11.9 Hz, *J* = 2.3 Hz), 3.66–3.59 (m, 1H), 3.58 (s, 6H), 3.56–3.46 (m, 1H), 3.33–3.21 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8, 141.2, 140.8, 140.7, 140.3, 135.3, 135.1, 133.8, 132.52, 135.50, 131.9, 130.2, 129.6, 129.4, 128.4, 128.3, 128.14, 128.10, 128.07, 127.4, 127.02, 127.01, 126.8, 126.6, 126.5, 126.4, 126.2, 108.4, 104.7, 55.6, 33.4, 31.7.

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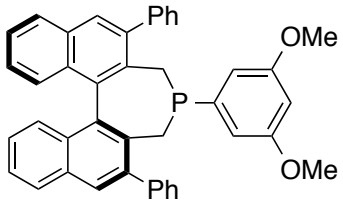
(1) Dvorak, C. A.; Liu, C. ; Shelton, J.; Kuei, C.; Sutton, S. W.; Lovenberg, T. W.; Carruthers, N. I. *ACS Med. Chem. Lett.* **2012**, *3*, 637–639.

(2) Ooi, T.; Kameda, M.; Maruoka, K. *J. Am. Chem. Soc.* **2003**, *125*, 5139–5151.

(3) Zhou, Y.-G.; Zhang, X. *Chem. Commun.* **2002**, 1124–1125.

^{31}P NMR (243 MHz, $CDCl_3$) δ 53.7.
FT-IR (film) 3055, 1588, 1416, 1206, 1158, 704 cm^{-1}.
LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{42}H_{34}O_3P$: 617, found: 617.
$[\alpha]^{25}_D$ = +12 (c = 1.0, $CDCl_3$).



(11b*S*)-4-(3,5-Dimethoxyphenyl)-2,6-diphenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine ((*S*)-4). The phosphine oxide (730 mg, 1.18 mmol) was added to a 100-mL round-bottom flask, which was then evacuated and back-filled with nitrogen (three cycles). Next, toluene (anhydrous; 24 mL) and Et_3N (1.15 mL) were added in turn. Cl_3SiH (Aldrich; 0.60 mL) was then added dropwise over 3 min, and the mixture was heated at 80 °C for 16 h. The mixture was allowed to cool to r.t., and then a solution of NaOH (10% in water; 50 mL) was added. This solution was stirred at r.t. for 30 min, and then the phases were separated. The aqueous layer was extracted with toluene (20 mL x 2), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue (a light-yellow solid) was dissolved in toluene (8.0 mL), and the mixture was filtered through a short pad of silica (eluent: toluene; 5.0 mL). The resulting solution was concentrated, which furnished the product as a white crystalline solid (700 mg, 99%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, 1H, *J* = 8.4 Hz), 7.89 (s, 1H), 7.85–7.81 (m, 1H), 7.67 (d, 2H, *J* = 7.5 Hz), 7.65 (s, 1H), 7.48–7.39 (m, 4H), 7.37–7.34 (m, 1H), 7.27–7.16 (m, 9H), 6.31 (t, 1H, *J* = 2.4 Hz), 5.91 (dd, 2H, *J* = 7.2 Hz, *J* = 2.4 Hz), 3.53 (s, 6H), 3.23 (dd, 1H, *J* = 14.7 Hz, *J* = 4.1 Hz), 2.94 (dd, 1H, *J* = 9.8 Hz, *J* = 12.5 Hz), 2.78–2.71 (m, 2H).

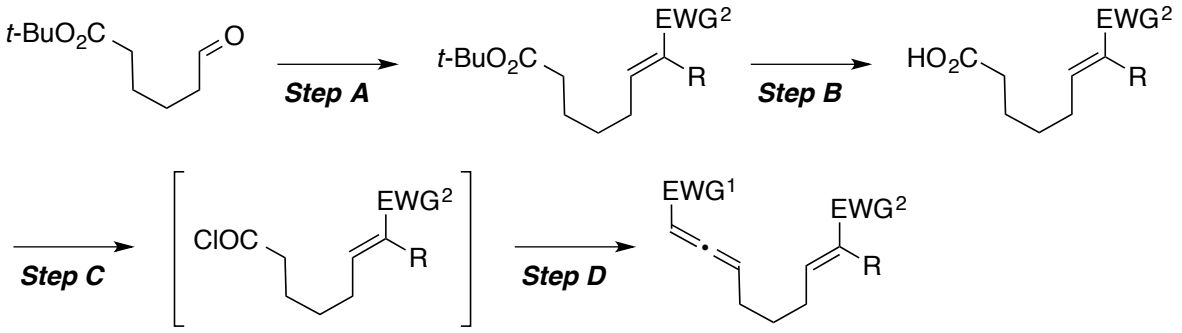
^{13}C NMR (151 MHz, $CDCl_3$) δ 160.5, 141.6, 141.4, 140.32, 140.29, 138.6, 134.9, 134.1, 132.3, 132.2, 131.9, 131.8, 131.4, 130.0, 129.7, 129.3, 128.9, 128.31, 128.30, 128.25, 127.3, 126.8, 126.7, 126.3, 126.10, 126.08, 125.7, 125.4, 108.8, 101.3, 55.3, 28.3, 25.6.

^{31}P NMR (243 MHz, $CDCl_3$) δ 6.2.
FT-IR (film) 2929, 1587, 1410, 1204, 1155, 703 cm^{-1}.
TOF-MS *m*/*z* $(M + H)^+$ calcd for $C_{42}H_{34}O_2P$: 601, found: 601.
$[\alpha]^{25}_D$ = –212 (c = 1.0, $CDCl_3$).

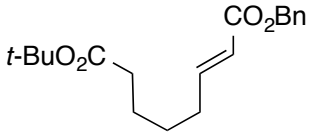
III. Preparation of Substrates

The yields in this section have not been optimized.

Substrates for entries 1–6 of Table 1 and entry 1 of Table 2.



General Procedure A (Step A). The appropriate phosphorane (1.2 equiv) was added to a round-bottom flask that contained *tert*-butyl 6-oxohexanoate (0.10 M; 1.0 equiv) in CH_2Cl_2. The resulting solution was stirred at r.t. for 12 h, and then it was concentrated under reduced pressure. The residue was then purified by column chromatography (hexanes→20% EtOAc in hexanes), which furnished the *E* olefin (yield generally greater than 80%; any *Z* isomer is separated at this stage).



1-Benzyl 8-(*tert*-butyl) (*E*)-oct-2-enedioate. The title compound was prepared according to General Procedure A, using benzyl 2-(triphenyl-λ^5-phosphanylidene)acetate, leading to a yellow oil (85%).

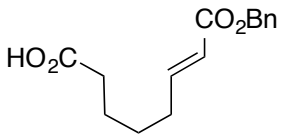
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.33 (m, 5H), 7.01 (dt, 1H, J = 15.8 Hz, J = 6.8 Hz), 5.89 (dt, 1H, J = 15.8 Hz, J = 1.7 Hz), 5.18 (s, 2H), 2.27–2.20 (m, 4H), 1.65–1.59 (m, 2H), 1.52–1.48 (m, 2H), 1.45 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 166.5, 149.4, 136.4, 128.7, 128.31, 128.26, 121.5, 80.3, 66.2, 35.4, 32.0, 28.3, 27.6, 24.7.

FT-IR (film) 2934, 1726, 1654, 1367, 1261, 1161, 981, 697 cm^{-1}.

TOF-MS m/z $(M + NH_4)^+$ calcd for $C_{19}H_{30}NO_4$: 336, found: 336.

General Procedure B (Step B). The *tert*-butyl ester and TFA (3 volumes relative to the *tert*-butyl ester) were added to a round-bottom flask, and the reaction mixture was stirred at r.t. for 12 h. Next, toluene was added (3 volumes relative to TFA), and the mixture was then concentrated under reduced pressure to remove the TFA. This residue was purified by column chromatography (20% EtOAc in hexanes→50% EtOAc in hexanes) (yield generally >70%).



(*E*)-8-(Benzyloxy)-8-oxooct-6-enoic acid. The title compound was prepared according to General Procedure B, using 1-benzyl 8-(*tert*-butyl) (*E*)-oct-2-enedioate, leading to a yellow oil (92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.68 (br s, 1H), 7.40–7.33 (m, 5H), 7.01 (dt, 1H, J = 15.8 Hz, J = 7.0 Hz), 5.90 (dt, 1H, J = 15.3 Hz, J = 1.7 Hz), 5.19 (s, 2H), 2.38 (t, 2H, J = 7.7 Hz), 2.27–2.20 (m, 2H), 1.71–1.65 (m, 2H), 1.57–1.51 (m, 2H).

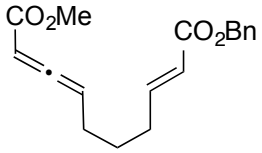
^{13}C NMR (125 MHz, $CDCl_3$) δ 179.5, 166.5, 149.2, 136.2, 128.7, 128.30, 128.27, 121.6, 66.2, 33.8, 31.9, 27.5, 24.2.

FT-IR (film) 2942, 1716, 1456, 1266, 981, 698 cm^{-1}.

LRMS (ESI) m/z $(M + H)^+$ calcd for $C_{15}H_{19}O_4$: 263, found: 263.

General Procedure C (Step C). The carboxylic acid (1.0 equiv) and a stir bar were placed in a round-bottom flask, which was then evacuated and back-filled with nitrogen (three cycles). CH_2Cl_2 (anhydrous; 10 volumes relative to the carboxylic acid) and dimethylformamide (0.10 equiv) were added in turn via syringe, and then the mixture was cooled to 0 °C. Next, oxalyl chloride (1.2 equiv) was added dropwise via syringe over 1 min. The reaction mixture was warmed to r.t. over 2 h, and then it was concentrated under reduced pressure. The residue was used in the next step without further purification.

General Procedure D (Step D). The appropriate phosphorane (1.0 equiv) and a stir bar were added to a round-bottom flask, which was then evacuated and back-filled with nitrogen (three cycles). Next, CH_2Cl_2 (anhydrous; 10 volumes relative to the acid chloride) was added via syringe, and then the mixture was cooled to 0 °C. Then, a solution of the acid chloride (0.10 M) in CH_2Cl_2 was added dropwise via syringe over 3 min, followed by triethylamine (1.2 equiv). The reaction mixture was allowed to slowly warm to r.t. over 4 h, and then it was concentrated under reduced pressure. The residue was purified by column chromatography.



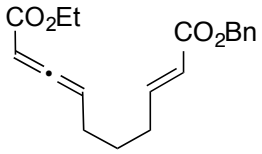
10-Benzyl 1-methyl (*E*)-deca-2,3,8-trienedioate. The title compound was synthesized according to General Procedure C/D from (*E*)-8-(benzyloxy)-8-oxooct-6-enoic acid, using methyl 2-(triphenyl-λ^5-phosphanylidene)acetate, leading to the title compound as a colorless oil (overall yield for 2 steps: 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.32 (m, 5H), 7.00 (dt, 1H, J = 15.9 Hz, J = 6.9 Hz), 5.90 (dt, 1H, J = 15.6 Hz, J = 1.6 Hz), 5.63–5.60 (m, 2H), 5.19 (s, 2H), 3.75 (s, 3H), 2.32–2.27 (m, 2H), 2.20–2.15 (m, 2H), 1.68–1.62 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6, 166.6, 166.4, 149.0, 136.3, 128.7, 128.33, 128.30, 121.8, 94.8, 88.5, 66.2, 52.1, 31.4, 27.0, 26.9.

FT-IR (neat) 2949, 1960, 1718, 1653, 1437, 1263, 1165, 1026 cm^{-1}.

LRMS (ESI) m/z $(M + H)^+$ calcd for $C_{18}H_{21}O_4$: 301, found: 301.



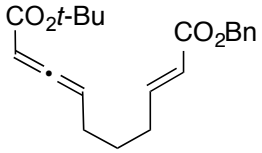
10-Benzyl 1-ethyl (*E*)-deca-2,3,8-trienedioate. The title compound was synthesized according to General Procedure C/D from (*E*)-8-(benzyloxy)-8-oxooct-6-enoic acid, using ethyl 2-(triphenyl-λ^5-phosphanylidene)acetate, leading to the title compound as a colorless oil (overall yield for 2 steps: 30%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.33 (m, 5H), 7.01 (dt, 1H, J = 15.4 Hz, J = 5.0 Hz), 5.90 (dt, 1H, J = 15.6 Hz, J = 1.0 Hz), 5.62–5.60 (m, 2H), 5.19 (s, 2H), 4.23–4.17 (m, 2H), 2.33–2.28 (m, 2H), 2.20–2.15 (m, 2H), 1.68–1.62 (m, 2H), 1.28 (t, 3H, J = 7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.5, 166.5, 166.2, 149.1, 136.3, 128.7, 128.33, 128.30, 121.8, 94.7, 88.9, 66.2, 61.0, 31.4, 27.04, 26.95, 14.4.

FT-IR (neat) 2937, 1960, 1718, 1653, 1262, 1173, 1028 cm^{-1}.

LRMS (ESI) m/z $(M + H)^+$ calcd for $C_{19}H_{23}O_4$: 315, found: 315.



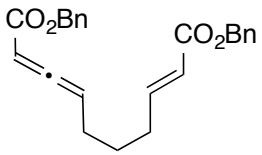
10-Benzyl 1-(*tert*-butyl) (*E*)-deca-2,3,8-trienedioate. The title compound was synthesized according to General Procedure C/D from (*E*)-8-(benzyloxy)-8-oxooct-6-enoic acid, using *tert*-butyl 2-(triphenyl-λ^5-phosphanylidene)acetate, leading to the title compound as a colorless oil (overall yield for 2 steps: 51%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.32 (m, 5H), 7.00 (dt, 1H, J = 15.5 Hz, J = 6.9 Hz), 5.90 (dt, 1H, J = 15.5 Hz, J = 1.5 Hz), 5.57–5.50 (m, 2H), 5.19 (s, 2H), 2.33–2.28 (m, 2H), 2.18–2.14 (m, 2H), 1.68–1.62 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.0, 166.5, 165.5, 149.2, 136.3, 128.7, 128.31, 128.29, 121.7, 94.4, 90.4, 81.0, 66.2, 31.4, 28.3, 27.1, 27.0.

FT-IR (neat) 2929, 1959, 1718, 1654, 1367, 1258, 1144, 1025 cm^{-1}.

LRMS (ESI) m/z $(M + H)^+$ calcd for $C_{21}H_{27}O_4$: 343, found: 343.



10-Benzyl 1-(*tert*-butyl) (*E*)-deca-2,3,8-trienedioate. The title compound was synthesized according to General Procedure C/D from (*E*)-8-(benzyloxy)-8-oxooct-6-enoic acid, using benzyl

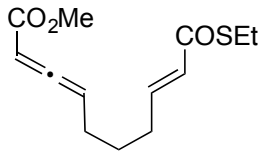
2-(triphenyl-λ^5-phosphanylidene)acetate, leading to the title compound as a colorless oil (overall yield for 2 steps: 31%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.27 (m, 10H), 6.97 (dt, 1H, *J* = 15.2 Hz, *J* = 6.8 Hz), 5.86 (dt, 1H, *J* = 15.9 Hz, *J* = 1.5 Hz), 5.67–5.61 (m, 2H), 5.22–5.15 (m, 4H), 2.28–2.24 (m, 2H), 2.20–2.15 (m, 2H), 1.66–1.59 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.8, 166.4, 165.9, 149.0, 136.4, 136.2, 128.69, 128.67, 128.34, 128.30, 128.29, 121.8, 94.9, 88.6, 66.7, 66.2, 31.4, 27.1, 26.9.

FT-IR (neat) 2931, 1959, 1716, 1654, 1454, 1258, 1148, 978 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{24}H_{25}O_4$: 377, found: 377.



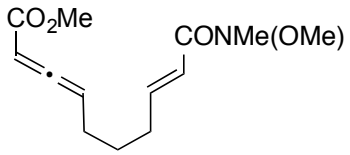
Methyl (*E*)-10-(ethylthio)-10-oxodeca-2,3,8-trienoate. The title compound was synthesized according to General Procedure C/D from (*E*)-8-(ethylthio)-8-oxooct-6-enoic acid, using methyl 2-(triphenyl-λ^5-phosphanylidene)acetate, leading to the title compound as a light-yellow oil (overall yield for 2 steps: 31%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (dt, 1H, *J* = 15.6 Hz, *J* = 6.8 Hz), 6.12 (dt, 1H, *J* = 15.5 Hz, *J* = 1.6 Hz), 5.64–5.59 (m, 2H), 3.75 (s, 3H), 2.95 (q, 2H, *J* = 7.5 Hz), 2.31–2.26 (m, 2H), 2.20–2.15 (m, 2H), 1.69–1.63 (m, 2H), 1.28 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6, 190.1, 166.5, 144.2, 129.5, 94.8, 88.5, 52.1, 31.3, 27.1, 27.0, 23.2, 14.9.

FT-IR (neat) 2931, 1960, 1719, 1669, 1632, 1437, 1260, 1162, 1031 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{13}H_{19}O_3S$: 255, found: 255.



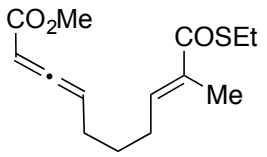
Methyl (*E*)-10-(methoxy(methyl)amino)-10-oxodeca-2,3,8-trienoate. The title compound was synthesized according to General Procedure C/D from (*E*)-8-(methoxy(methyl)amino)-8-oxooct-6-enoic acid, using methyl 2-(triphenyl-λ^5-phosphanylidene)acetate, leading to the title compound as a colorless oil (overall yield for 2 steps: 64%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (dt, 1H, *J* = 15.7 Hz, *J* = 6.9 Hz), 6.42 (d, 1H, *J* = 15.5 Hz), 5.63–5.61 (m, 2H), 3.74 (s, 3H), 3.70 (s, 3H), 3.25 (s, 3H), 2.35–2.30 (m, 2H), 2.21–2.16 (m, 2H), 1.69–1.63 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6, 167.1, 166.6, 146.8, 120.0, 94.9, 88.4, 61.8, 52.1, 32.5, 31.6, 27.4, 27.0.

FT-IR (neat) 2938, 1959, 1720, 1663, 1632, 1438, 1260, 1164, 987 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{13}H_{20}NO_4$: 254, found: 254.



Methyl (*E*)-10-(ethylthio)-9-methyl-10-oxodeca-2,3,8-trienoate. The title compound was synthesized according to General Procedure C/D from (*E*)-8-(ethylthio)-7-methyl-8-oxooct-6-enoic acid, using methyl 2-(triphenyl-λ^5-phosphanylidene)acetate, leading to the title compound as a light-yellow oil (overall yield for 2 steps: 32%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.72–6.68 (m, 1H), 5.65–5.62 (m, 2H), 3.74 (s, 3H), 2.92 (q, 2H, *J* = 7.2 Hz), 2.31–2.25 (m, 2H), 2.21–2.16 (m, 2H), 1.88 (s, 3H), 1.68–1.61 (m, 2H), 1.27 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.5, 193.9, 166.6, 139.7, 136.7, 94.9, 88.5, 52.2, 27.9, 27.5, 27.1, 23.4, 14.9, 12.6.

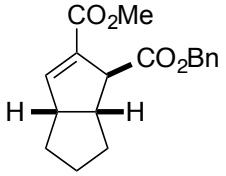
FT-IR (neat) 2924, 1961, 1723, 1654, 1437, 1260, 1161 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{14}H_{21}O_3S$: 269, found: 269.

IV. Enantioselective Intramolecular [3 + 2] Cycloadditions

General Procedure. The phosphine catalyst (0.10 equiv) was added to an oven-dried 20-mL vial equipped with a stir bar. This vial was capped with a septum-lined cap, the joint was covered with electrical tape, and then the vial was evacuated and back-filled with nitrogen (three cycles). The substrate (1.00 equiv) was added to a separate vial, which was then capped with a septum-lined cap, the joint was covered with electrical tape, and then the vial was evacuated and back-filled with nitrogen (three cycles). Next, toluene (anhydrous) was added to the vial that contained the substrate. This solution was added via syringe to the vial that contained the catalyst (under a positive pressure of nitrogen). Next, the reaction vial was detached from the nitrogen manifold, and grease was applied to the puncture hole in the septum in order to impede moisture/air from entering the vial. The reaction mixture was stirred at room temperature for 24 h, and then an aqueous solution of hydrogen peroxide (10%; 1.0 mL) was added. The resulting mixture was stirred for 10 min, and then an aqueous solution of $Na_2S_2O_3$ (saturated; 2.0 mL) was added. The mixture was stirred for 10 min, and then the aqueous layer was extracted with EtOAc (5 mL x 3), and the combined organic layers were dried over $MgSO_4$ and then concentrated under reduced pressure. The resulting residue was purified by column chromatography.

Note: Because the purity of the substrate can have a significant impact on the course of the reaction, the substrate was generally purified by column chromatography prior (<7 days) to carrying out the [3+2] cycloaddition.



1-Benzyl 2-methyl (1*S*,3a*S*,6a*R*)-1,3a,4,5,6,6a-hexahydropentalene-1,2-dicarboxylate (Table 1, entry 1). This compound was prepared according to the General Procedure, using 10-benzyl 1-methyl (*E*)-deca-2,3,8-trienedioate (135 mg, 0.45 mmol), (*S*)-**4** (27.0 mg, 0.045 mmol), and toluene (4.5 mL). After purification by column chromatography (eluted with hexanes→20% Et_2O and then 20% acetone in hexanes), the title compound was isolated as a colorless oil (109 mg, 81% yield) with 98% ee.

HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 3% 2-propanol in hexanes; 1.0 mL/min; retention times: 14.3 min (minor), 15.6 min (major).

The second run was performed with (*R*)-**4**. The product was isolated as a colorless oil (114 mg, 84% yield) with 96% ee.

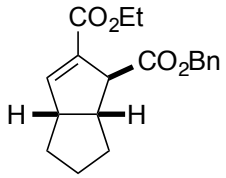
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.30 (m, 5H), 6.76 (dd, 1H, J = 1.8 Hz, J = 2.8 Hz), 5.15 (s, 2H), 3.65 (s, 3H), 3.53–3.51 (m, 1H), 3.44–3.38 (m, 1H), 2.85–2.80 (m, 1H), 1.87–1.81 (m, 1H), 1.76–1.71 (m, 1H), 1.58–1.48 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 164.8, 149.9, 136.4, 133.3, 128.4, 128.0, 127.9, 66.5, 57.6, 51.6, 50.7, 47.3, 34.9, 30.9, 25.3.

FT-IR (neat) 2949, 1718, 1635, 1437, 1266, 1163, 1101, 1012 cm^{-1}.

LRMS (ESI) m/z $(M + H)^+$ calcd for $C_{18}H_{21}O_4$: 301, found: 301.

$[\alpha]^{25}_D$ = –94 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



1-Benzyl 2-ethyl (1*S*,3a*S*,6a*R*)-1,3a,4,5,6,6a-hexahydropentalene-1,2-dicarboxylate (Table 1, entry 2). The title compound was prepared according to the General Procedure, using 10-benzyl 1-ethyl (*E*)-deca-2,3,8-trienedioate (142 mg, 0.45 mmol), (*S*)-**4** (27.0 mg, 0.045 mmol), and toluene (4.5 mL). After purification by column chromatography (eluted with hexanes→20% Et_2O and then 20% acetone in hexanes), the title compound was isolated as a colorless oil (120 mg, 85% yield) with 98% ee.

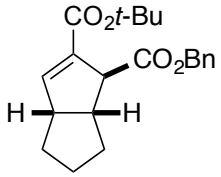
HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 3% 2-propanol in hexanes; 1.0 mL/min; retention times: 12.1 min (minor), 14.3 min (major).

The second run was performed with (*R*)-**4**. The product was isolated as a colorless oil (122 mg, 86% yield) with 97% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.32 (m, 5H), 6.77 (s, 1H), 5.16 (s, 2H), 4.16–4.11 (m, 2H), 3.54 (s, 1H), 3.44–3.40 (m, 1H), 2.86–2.82 (m, 1H), 1.89–1.82 (m, 1H), 1.79–1.70 (m, 1H), 1.60–1.49 (m, 4H), 1.21 (t, 3H, J = 7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 164.4, 149.6, 136.4, 133.6, 128.6, 128.2, 128.1, 66.5, 60.5, 57.6, 50.7, 47.3, 34.9, 30.9, 25.3, 14.3.

FT-IR (neat) 2951, 1718, 1636, 1372, 1263, 1162, 1098, 1021 cm^{-1}.
LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{19}H_{23}O_4$: 315, found: 315.
$[\alpha]^{25}_D$ = –85 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



1-Benzyl 2-(*tert*-butyl) (1*S*,3a*S*,6a*R*)-1,3a,4,5,6,6a-hexahydropentalene-1,2-dicarboxylate (Table 1, entry 3). The title compound was prepared according to the General Procedure, using 10-benzyl 1-(*tert*-butyl) (*E*)-deca-2,3,8-trienedioate (137 mg, 0.40 mmol), (*S*)-**4** (24.0 mg, 0.040 mmol), and toluene (4.0 mL). After purification by column chromatography (eluted with hexanes→20% Et_2O and then 20% acetone in hexanes), the title compound was isolated as a colorless oil (114 mg, 83% yield) with 97% ee.

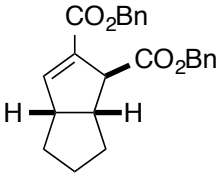
HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 3% 2-propanol in hexanes; 1.0 mL/min; retention times: 9.5 min (minor), 12.1 min (major).

The second run was performed with (*R*)-**4**. The product was isolated as a colorless oil (116 mg, 85% yield) with 98% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.31 (m, 5H), 6.68 (dd, 1H, *J* = 1.5 Hz, *J* = 2.5 Hz), 5.20–5.10 (m, 2H), 3.49–3.47 (m, 1H), 3.41–3.38 (m, 1H), 2.84–2.79 (m, 1H), 1.87–1.80 (m, 1H), 1.77–1.68 (m, 1H), 1.59–1.48 (m, 4H), 1.42 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 163.7, 148.8, 136.3, 135.0, 128.6, 128.2 (2), 80.8, 66.5, 57.6, 50.5, 47.3, 35.0, 30.9, 28.2, 25.3.

FT-IR (neat) 2951, 1735, 1709, 1367, 1271, 1163, 1101 cm^{-1}.
LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{21}H_{27}O_4$: 343, found: 343.
$[\alpha]^{25}_D$ = –78 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



Dibenzyl (1*S*,3a*S*,6a*R*)-1,3a,4,5,6,6a-hexahydropentalene-1,2-dicarboxylate (Table 1, entry 4). The title compound was prepared according to the General Procedure, using 10-benzyl 1-benzyl (*E*)-deca-2,3,8-trienedioate (140 mg, 0.37 mmol), (*S*)-**4** (22.0 mg, 0.037 mmol), and toluene (3.7 mL). After purification by column chromatography (eluted with hexanes→20% Et_2O in hexanes), the title compound was isolated as a colorless oil (125 mg, 89% yield) with 98% ee.

HPLC analysis of the product: Daicel CHIRALPAK IB column; solvent system: 10% 2-propanol in hexanes; 1.0 mL/min; retention times: 8.9 min (minor), 11.3 min (major).

The second run was performed with (*R*)-**4**. The product was isolated as a colorless oil (128 mg, 91% yield) with 98% ee.

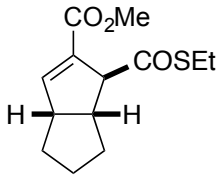
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.29 (m, 10H), 6.83 (dd, 1H, *J* = 1.5 Hz, *J* = 2.5 Hz), 5.13 (s, 2H), 5.10 (d, 2H, *J* = 8.1 Hz), 3.56 (td, 1H, *J* = 3.0 Hz, *J* = 1.6 Hz), 3.45–3.40 (m, 1H), 2.87–2.82 (m, 1H), 1.89–1.80 (m, 1H), 1.76–1.69 (m, 1H), 1.59–1.50 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 164.1, 150.4, 136.3, 136.2, 133.3, 128.63, 128.61, 128.22, 128.17, 128.1, 66.6, 66.3, 57.5, 50.8, 47.4, 34.9, 30.9, 25.4.

FT-IR (neat) 2950, 1718, 1636, 1454, 1262, 1164, 1089, 1011 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{24}H_{25}O_4$: 377, found: 377.

$[\alpha]^{25}_D$ = –68 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



Methyl (1*S*,3a*S*,6a*R*)-1-((ethylthio)carbonyl)-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate (Table 1, entry 5). The title compound was prepared according to the General Procedure, using methyl (*E*)-10-(ethylthio)-10-oxodeca-2,3,8-trienoate (114 mg, 0.45 mmol), (*S*)-**4** (27.0 mg, 0.045 mmol), and toluene (4.5 mL). After purification by column chromatography (eluted with hexanes→20% Et_2O and then 20% acetone in hexanes), the title compound was isolated as a colorless oil (99 mg, 87% yield) with 91% ee.

HPLC analysis of the product: Daicel CHIRALPAK AS-H column; solvent system: 5% 2-propanol in hexanes; 1.0 mL/min; retention times: 6.1 min (minor), 7.5 min (major).

The second run was performed with (*R*)-**4**. The product was isolated as a colorless oil (102 mg, 89% yield) with 94% ee.

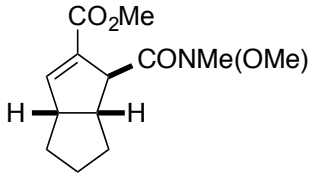
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (dd, 1H, *J* = 1.4 Hz, *J* = 2.5 Hz), 3.73 (s, 3H), 3.68–3.67 (m, 1H), 3.47–3.42 (m, 1H), 2.88 (qd, 2H, *J* = 7.4 Hz, *J* = 1.0 Hz), 2.80–2.76 (m, 1H), 1.90–1.85 (m, 1H), 1.78–1.73 (m, 1H), 1.59–1.49 (m, 4H), 1.25 (t, 3H, *J* = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 200.9, 164.6, 151.5, 133.0, 66.0, 51.7, 50.6, 48.1, 34.9, 30.8, 25.2, 23.4, 14.7.

FT-IR (neat) 2950, 1721, 1685, 1437, 1265, 1088, 1023 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{13}H_{19}O_3S$: 255, found: 255.

$[\alpha]^{25}_D$ = –180 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



Methyl (1*S*,3a*S*,6a*R*)-1-(methoxy(methyl)carbamoyl)-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate (Table 1, entry 6). The title compound was prepared according to the General Procedure, using methyl (*E*)-10-(methoxy(methyl)amino)-10-oxodeca-2,3,8-trienoate (114 mg, 0.45 mmol), (*S*)-**4** (27.0 mg, 0.045 mmol), and toluene (4.5 mL). After purification by column

chromatography (eluted with 20% EtOAc in hexanes→50% EtOAc in hexanes) and preparative HPLC (IA column; solvent system: 20% EtOAc in hexanes; no separation of the enantiomers of the product), the title compound was isolated as a colorless oil (82 mg, 72% yield) with 97% ee.

HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: 10% 2-propanol in hexanes; 1.0 mL/min; retention times: 7.3 min (major), 8.7 min (minor).

The second run was performed with (*R*)-**4**. The product was isolated as a colorless oil (88 mg, 77% yield) with 97% ee.

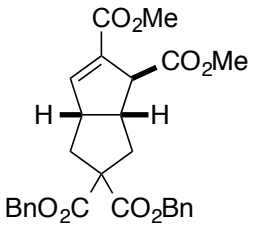
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (dd, 1H, *J* = 2.5 Hz, *J* = 2.4 Hz), 3.92 (s, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.47–3.43 (m, 1H), 3.24 (s, 3H), 2.74–2.69 (m, 1H), 1.88–1.81 (m, 1H), 1.76–1.72 (m, 1H), 1.61–1.49 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 149.9, 133.7, 61.4, 54.3, 51.7, 50.9, 47.1, 35.2, 31.1, 25.4.

FT-IR (neat) 2950, 1717, 1661, 1439, 1355, 1267, 1104 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{13}H_{20}NO_4$: 254, found: 254.

$[\alpha]^{25}_D$ = –107 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



5,5-Dibenzyl 1,2-dimethyl (1*S*,3a*S*,6a*R*)-3a,4,6,6a-tetrahydropentalene-1,2,5,5(1*H*)-tetracarboxylate (Table 1, entry 7). The title compound was prepared according to the General Procedure, using 4,4-dibenzyl 1,8-dimethyl (*E*)-octa-1,6,7-triene-1,4,4,8-tetracarboxylate (123 mg, 0.25 mmol), (*S*)-**4** (15.0 mg, 0.025 mmol), and toluene (2.5 mL). Reaction temperature: 40 °C. After purification by column chromatography (eluted with hexanes→40% Et_2OAc in hexanes), the title compound was isolated as a colorless oil (108 mg, 88% yield) with 96% ee.

HPLC analysis of the product: Daicel CHIRALPAK IA column; solvent system: 10% 2-propanol in hexanes; 1.0 mL/min; retention times: 19.6 min (minor), 20.8 min (major).

The second run was performed with (*R*)-**4**. The product was isolated as a colorless oil (107 mg, 87% yield) with 97% ee.

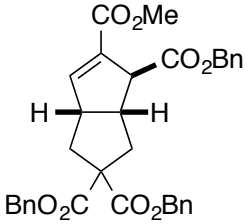
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.31 (m, 6H), 7.26–7.22 (m, 4H), 6.76 (dd, 1H, *J* = 2.4 Hz, *J* = 1.4 Hz), 5.16–5.04 (m, 4H), 3.74 (s, 3H), 3.69 (s, 3H), 3.63–3.61 (m, 1H), 3.59–3.54 (m, 1H), 2.91 (qd, 1H, *J* = 8.1 Hz, *J* = 2.5 Hz), 2.68–2.59 (m, 2H), 2.11–2.07 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 171.2, 170.6, 164.5, 148.4, 135.50, 135.47, 133.0, 128.71, 128.69, 128.49, 128.46, 128.2, 128.1, 67.53, 67.47, 61.4, 56.0, 52.3, 51.8, 50.0, 46.3, 41.0, 37.8.

FT-IR (neat) 2950, 1730, 1496, 1437, 1240, 1165, 1104, 1027 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{28}H_{29}O_8$: 493, found: 493.

$[\alpha]^{25}_D$ = –74 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



1,5,5-Tribenzyl 2-methyl (1*S*,3a*S*,6a*R*)-3a,4,6,6a-tetrahydropentalene-1,2,5,5(1*H*)-tetracarboxylate (Table 1, entry 8). The title compound was prepared according to the General Procedure, using 1,4,4-tribenzyl 8-methyl (*E*)-octa-1,6,7-triene-1,4,4,8-tetracarboxylate (142 mg, 0.25 mmol), (*S*)-**4** (15.0 mg, 0.025 mmol), and toluene (2.5 mL). After purification by column chromatography (eluted with hexanes→30% EtOAc in hexanes), the title compound was isolated as a colorless oil (128 mg, 90% yield) with 95% ee.

HPLC analysis of the product: Daicel CHIRALPAK IA column; solvent system: 15% 2-propanol in hexanes; 1.0 mL/min; retention times: 25.9 min (minor), 31.1 min (major).

The second run was performed with (*R*)-**4**. The product was isolated as a colorless oil (121 mg, 85% yield) with 94% ee.

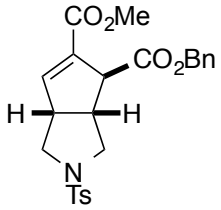
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.30 (m, 11H), 7.26–7.22 (m, 4H), 6.76 (dd, 1H, *J* = 2.4 Hz, *J* = 1.5 Hz), 5.13 (d, 2H, *J* = 2.7 Hz), 5.12 (d, 2H, *J* = 4.9 Hz), 5.06 (d, 2H, *J* = 3.7 Hz), 3.68–3.67 (m, 1H), 3.66 (s, 3H), 3.59–3.54 (m, 1H), 3.00–2.90 (m, 1H), 2.67–2.59 (m, 2H), 2.14–2.09 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 171.1, 170.6, 164.4, 148.4, 136.1, 135.5, 133.1, 128.71, 128.69, 128.65, 128.49, 128.46, 128.3, 128.2, 128.12, 128.10, 67.54, 67.48, 66.8, 61.4, 56.3, 51.8, 50.0, 46.3, 41.0, 37.8, 30.5.

FT-IR (neat) 2950, 1729, 1455, 1242, 1165, 1105, 1028 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{34}H_{33}O_8$: 569, found: 569.

$[\alpha]^{25}_D$ = –68 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



4-Benzyl 5-methyl (3a*R*,4*S*,6a*R*)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole-4,5-dicarboxylate (Table 1, entry 9). The title compound was prepared according to the General Procedure, using methyl (*E*)-5-((*N*-(4-(benzyloxy)-4-oxobut-2-en-1-yl)-4-methylphenyl)sulfonamido)penta-2,3-dienoate (137 mg, 0.30 mmol), (*S*)-**4** (18.0 mg, 0.030 mmol), and toluene (3.0 mL). After purification by column chromatography (eluted with 10% EtOAc in hexanes→30% EtOAc in hexanes), the title compound was isolated as a sticky white solid (131 mg, 96% yield) with 94% ee.

HPLC analysis of the product: Daicel CHIRALPAK IA column; solvent system: 40% 2-propanol in hexanes; 1.0 mL/min; retention times: 13.4 min (minor), 22.1 min (major).

The second run was performed with (*R*)-**4**. The product was isolated as a sticky white solid (129 mg, 94% yield) with 93% ee.

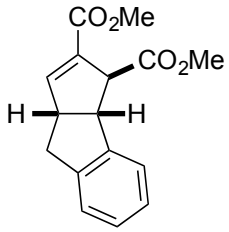
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68–7.66 (m, 2H), 7.39–7.30 (m, 7H), 6.66 (t, 1H, *J* = 2.0 Hz), 5.13 (d, 2H, *J* = 1.6 Hz), 3.70–3.69 (m, 1H), 3.67 (s, 3H), 3.57–3.52 (m, 1H), 3.24–3.16 (m, 3H), 3.08 (dd, 1H, *J* = 10.0 Hz, *J* = 8.3 Hz), 3.01–2.95 (m, 1H), 2.45 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 163.9, 145.5, 144.1, 135.8, 135.3, 129.8, 128.7, 128.4, 128.2, 128.1, 127.3, 67.0, 56.1, 54.5, 51.8, 51.3, 49.8, 45.9, 21.7.

FT-IR (neat) 2950, 1735, 1437, 1346, 1270, 1162, 1013, 663 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{24}H_{26}NO_6S$: 456, found: 456.

$[\alpha]^{25}_D$ = –58 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



Dimethyl (3*S*,3a*R*,8a*R*)-3,3a,8,8a-tetrahydrocyclopenta[*a*]indene-2,3-dicarboxylate (Table 1, entry 10). The title compound was prepared according to the General Procedure, using methyl (*E*)-5-(2-(3-methoxy-3-oxoprop-1-en-1-yl)phenyl)penta-2,3-dienoate (49 mg, 0.18 mmol), (*S*)-**2** (14.0 mg, 0.036 mmol), and toluene (1.8 mL). After purification by column chromatography (eluted with 5% EtOAc in hexanes→20% EtOAc in hexanes), the title compound was isolated as a colorless oil (39 mg, 80% yield) with 86% ee.

HPLC analysis of the product: Daicel CHIRALCEL OD-H column; solvent system: 10% 2-propanol in hexanes; 1.0 mL/min; retention times: 8.5 min (major), 26.1 min (minor).

The second run was performed with (*R*)-**2**. The product was isolated as a sticky white solid (41 mg, 84% yield) with 86% ee.

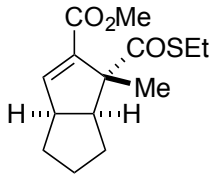
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.36 (m, 1H), 7.27–7.20 (m, 3H), 6.85 (dd, 1H, *J* = 2.2 Hz, *J* = 1.4 Hz), 4.05–4.03 (m, 1H), 3.94–3.91 (m, 1H), 3.91–3.86 (m, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.28 (dd, 1H, *J* = 16.2 Hz, *J* = 9.2 Hz), 2.98 (dd, 1H, *J* = 16.2 Hz, *J* = 2.6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 164.6, 149.8, 144.4, 141.3, 133.3, 127.8, 127.3, 125.2, 124.7, 57.1, 53.5, 52.5, 51.8, 49.2, 36.4.

FT-IR (neat) 2952, 1737, 1437, 1346, 1256, 1173, 1097 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{16}H_{17}O_4$: 273, found: 273.

$[\alpha]^{25}_D$ = +40 (c = 1.0, $CHCl_3$; obtained with (*R*)-**2**).



Methyl (1*R*,3a*S*,6a*S*)-1-((ethylthio)carbonyl)-1-methyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate (Table 2, entry 1). The title compound was prepared according to the General Procedure, using methyl (*E*)-10-(ethylthio)-9-methyl-10-oxodeca-2,3,8-trienoate (121 mg, 0.45

mmol), (*S*)-**1** (33.0 mg, 0.090 mmol), and toluene (4.5 mL). After purification by column chromatography (eluted with hexanes→20% Et_2O and then 20% acetone in hexanes), the title compound was isolated as a colorless oil (68 mg, 56% yield) with 97% ee.

HPLC analysis of the product: Daicel CHIRALCEL OD-H column; solvent system: 5% 2-propanol in hexanes; 1.0 mL/min; retention times: 5.8 min (major), 12.3 min (minor).

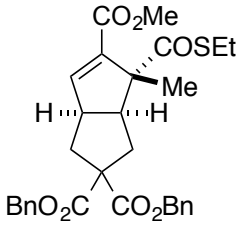
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (d, 1H, *J* = 2.4 Hz), 3.73 (s, 3H), 3.45–3.40 (m, 1H), 2.88–2.75 (m, 3H), 1.89–1.81 (m, 1H), 1.65–1.49 (m, 5H), 1.47 (s, 3H), 1.22 (t, 3H, *J* = 7.4 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 204.4, 164.7, 152.3, 137.0, 64.0, 52.7, 51.6, 49.2, 30.7, 29.1, 26.5, 23.6, 17.8, 14.6.

FT-IR (neat) 2951, 1721, 1683, 1436, 1262, 1061, 967, 793 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{14}H_{21}O_3S$: 269, found: 269.

$[\alpha]^{25}_D$ = +192 (c = 1.0, $CHCl_3$; obtained with (*S*)-**1**).



2,2-Dibenzyl 5-methyl (3a*S*,4*R*,6a*S*)-4-((ethylthio)carbonyl)-4-methyl-3,3a,4,6a-tetrahydropentalene-2,2,5(1*H*)-tricarboxylate (Table 2, entry 2). The title compound was prepared according to the General Procedure, using 5,5-dibenzyl 1-methyl (*E*)-9-(ethylthio)-8-methyl-9-oxonona-1,2,7-triene-1,5,5-tricarboxylate (97 mg, 0.18 mmol), (*R*)-**4** (11.0 mg, 0.018 mmol), and toluene (1.8 mL). Reaction time: 48 h. After purification by column chromatography (eluted with hexanes→30% EtOAc in hexanes), the title compound was isolated as a colorless oil (89 mg, 92% yield) with 98% ee.

HPLC analysis of the product: Daicel CHIRALCEL OD-H column; solvent system: 10% 2-propanol in hexanes; 1.0 mL/min; retention times: 11.6 min (minor), 16.5 min (major).

The second run was performed with (*S*)-**4**. The product was isolated as a colorless oil (90 mg, 93% yield) with 98% ee.

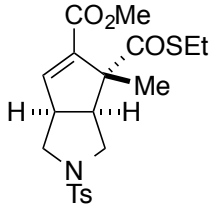
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.31 (m, 6H), 7.26–7.22 (m, 4H), 6.76 (dd, 1H, *J* = 2.4 Hz, *J* = 1.4 Hz), 5.16–5.04 (m, 4H), 3.74 (s, 3H), 3.54–3.49 (m, 1H), 2.87–2.79 (m, 3H), 2.73 (ddd, 1H, *J* = 13.4 Hz, *J* = 9.4 Hz, *J* = 1.9 Hz), 2.39 (ddd, 1H, *J* = 13.3 Hz, *J* = 7.7 Hz, *J* = 1.6 Hz), 2.11 (dd, 1H, *J* = 12.6 Hz, *J* = 11.2 Hz), 1.96 (dd, 1H, *J* = 13.1 Hz, *J* = 6.8 Hz), 1.49 (s, 3H), 1.21 (t, 3H, *J* = 7.4 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 203.4, 171.1, 170.7, 164.4, 150.7, 136.8, 135.5, 128.73, 128.72, 128.51, 128.49, 128.2, 67.6, 67.5, 64.0, 61.5, 51.8, 51.7, 47.9, 37.6, 35.9, 23.8, 17.8, 14.5.

FT-IR (neat) 2951, 1724, 1676, 1454, 1238, 1172, 1066, 966 cm^{-1}.

MS (ESI + APCI) *m*/*z* $(M + Na)^+$ calcd for $C_{30}H_{32}O_7SNa$: 559, found: 559.

$[\alpha]^{25}_D$ = –146 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



Methyl (3a*S*,4*R*,6a*S*)-4-((ethylthio)carbonyl)-4-methyl-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole-5-carboxylate (Table 2, entry 3). The title compound was prepared according to the General Procedure, using methyl (*E*)-5-((*N*-(4-(ethylthio)-3-methyl-4-oxobut-2-en-1-yl)-4-methylphenyl)sulfonamido)penta-2,3-dienoate (127 mg, 0.30 mmol), (*S*)-**1** (11.0 mg, 0.030 mmol), and toluene (3.0 mL). After purification by column chromatography (eluted with 10% EtOAc in hexanes→30% EtOAc in hexanes), the title compound was isolated as a sticky yellow solid (97 mg, 76% yield) with 94% ee.

HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 40% 2-propanol in hexanes; 1.0 mL/min; retention times: 13.2 min (major), 23.4 min (minor).

The second run was performed with (*S*)-**1**. The product was isolated as a sticky yellow solid (110 mg, 80% yield) with 94% ee.

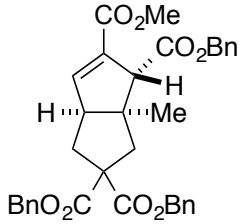
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, 2H, *J* = 8.0 Hz), 7.35 (d, 2H, *J* = 8.2 Hz), 6.80 (d, 1H, *J* = 2.5 Hz), 3.74 (s, 3H), 3.54 (tt, 1H, *J* = 8.4 Hz, *J* = 2.8 Hz), 3.38 (dd, 1H, *J* = 9.5 Hz, *J* = 3.5 Hz), 3.26 (dd, 1H, *J* = 10.0 Hz, *J* = 3.0 Hz), 3.04 (t, 1H, *J* = 9.4 Hz), 2.97–2.87 (m, 2H), 2.86–2.78 (m, 2H), 2.45 (s, 3H), 1.53 (s, 3H), 1.20 (t, 3H, *J* = 7.4 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 203.1, 163.8, 147.2, 144.1, 139.6, 131.8, 129.9, 128.2, 63.9, 51.9, 51.4, 50.8, 49.5, 48.3, 23.7, 21.7, 17.7, 14.5.

FT-IR (neat) 2950, 1718, 1675, 1345, 1163, 967 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{20}H_{26}NO_5S_2$: 424, found: 424.

$[\alpha]^{25}_D$ = +97 (c = 1.0, $CHCl_3$; obtained with (*S*)-**1**).



1,5,5-Tribenzyl 2-methyl (1*R*,3a*S*,6a*S*)-6a-methyl-3a,4,6,6a-tetrahydropentalene-1,2,5,5(1*H*)-tetracarboxylate (Table 2, entry 4). The title compound was prepared according to the General Procedure, using 1,4,4-tribenzyl 8-methyl (*E*)-2-methylocta-1,6,7-triene-1,4,4,8-tetracarboxylate (117 mg, 0.20 mmol), (*S*)-**2** (7.8 mg, 0.020 mmol), and toluene (2.0 mL). After purification by column chromatography (eluted with hexanes→30% Et_2OAc in hexanes), the title compound was isolated as a colorless oil (108 mg, 92% yield) with 90% ee.

HPLC analysis of the product: Daicel CHIRALPAK IA column; solvent system: 15% 2-propanol in hexanes; 1.0 mL/min; retention times: 24.5 min (minor), 30.9 min (major).

The second run was performed with (*R*)-**2**. The product was isolated as a colorless oil (112 mg, 96% yield) with 89% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.30 (m, 11H), 7.24–7.22 (m, 4H), 6.71 (dd, 1H, *J* = 2.3 Hz, *J* = 1.4 Hz), 5.14 (d, 2H, *J* = 2.6 Hz), 5.10 (d, 2H, *J* = 4.1 Hz), 5.03 (s, 2H), 3.75 (dd, 1H, *J* = 2.6 Hz, *J* = 1.5 Hz), 3.65 (s, 3H), 3.08 (dq, 1H, *J* = 8.5 Hz, *J* = 2.9 Hz), 2.61–2.56 (m, 2H), 2.42–2.35 (m, 2H), 1.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 171.7, 171.1, 164.4, 148.6, 136.0, 135.5, 133.6, 128.71, 128.69, 128.65, 128.63, 128.57, 128.51, 128.47, 128.34, 128.31, 128.2, 67.62, 67.60, 66.6, 61.6, 61.2, 58.0, 53.2, 51.7, 49.3, 37.3, 23.4.

FT-IR (neat) 2952, 1730, 1498, 1456, 1332, 1248, 1171, 751 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{35}H_{35}O_8$: 583, found: 583.

$[\alpha]^{25}_D$ = –98 (c = 1.0, $CHCl_3$; obtained with (*S*)-**2**).

***S*-Ethyl (1*R*,9b*R*)-4-oxo-1,2,4,9b-tetrahydrocyclopenta[*c*]chromene-1-carbothioate (eq 5).** The title compound was prepared according to the General Procedure, using (*E*)-2-(3-(ethylthio)-3-oxoprop-1-en-1-yl)phenyl buta-2,3-dienoate (123 mg, 0.45 mmol), (*S*)-**3** (27.0 mg, 0.045 mmol), and toluene (4.5 mL). After purification by column chromatography (eluted with hexanes→20% EtOAc in hexanes), the title compound was isolated as a light-yellow solid (105 mg, 85% yield) with 96% ee.

HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 5% 2-propanol in hexanes; 1.0 mL/min; retention times: 13.2 min (major), 14.6 min (minor).

The second run was performed with (*R*)-**3**. The product was isolated as a yellow solid (109 mg, 88% yield) with 95% ee.

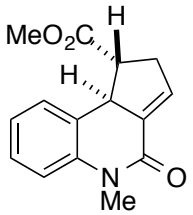
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.23 (m, 2H), 7.16 (td, 1H, *J* = 7.5 Hz, *J* = 1.5 Hz), 7.09 (dd, 1H, *J* = 8.0 Hz, *J* = 1.5 Hz), 6.91 (q, 1H, *J* = 5 Hz), 4.65 (q, 1H, *J* = 5.0 Hz), 3.69 (q, 1H, *J* = 9.5 Hz), 3.10–3.03 (m, 3H), 2.98–2.94 (m, 1H), 1.36 (t, 3H, *J* = 7.7 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 200.1, 160.1, 150.9, 142.4, 130.7, 128.7, 126.3, 125.8, 125.1, 117.4, 60.5, 45.6, 38.6, 24.0, 14.8.

FT-IR (neat) 2929, 1754, 1678, 1452, 1222, 1180, 1069, 967, 756 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{15}H_{15}O_3S$: 275, found: 275.

$[\alpha]^{25}_D$ = –114 (c = 1.0, $CHCl_3$; obtained with (*S*)-**3**).



Methyl (1*R*,9b*R*)-5-methyl-4-oxo-2,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1-carboxylate (Table 3, entry 1). The title compound was prepared according to the General Procedure, using methyl (*E*)-3-(2-(*N*-methylbuta-2,3-dienamido)phenyl)acrylate (116 mg, 0.45 mmol), (*S*)-**4** (54.0 mg, 0.090 mmol), and toluene (9.0 mL). After purification by column chromatography (eluted with 20% EtOAc in hexanes→50% EtOAc in hexanes), the title compound was isolated as a white solid (104 mg, 90% yield) with 61% ee.

HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 20% 2-propanol in hexanes; 1.0 mL/min; retention times: 9.1 min (major), 13.8 min (minor).

The second run was performed with (*R*)-**4**. The product was isolated as a yellow solid (107 mg, 92% yield) with 70% ee.

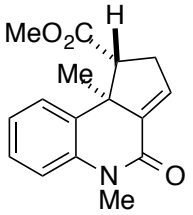
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.25 (m, 2H), 7.09 (td, 1H, *J* = 7.7 Hz, *J* = 0.9 Hz), 7.0 (d, 1H, *J* = 7.9 Hz), 6.67 (q, 1H, *J* = 2.8 Hz), 4.50–4.46 (m, 1H), 3.85 (s, 3H), 3.49 (q, 1H, *J* = 9.0 Hz), 3.41 (s, 3H), 3.01–2.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 162.0, 139.6, 136.8, 134.6, 128.5, 127.8, 125.9, 123.4, 114.9, 52.6, 51.1, 47.1, 37.1, 29.7.

FT-IR (neat) 2951, 1733, 1661, 1600, 1456, 1353, 1276, 1218, 755 cm^{-1}.

LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{15}H_{16}NO_3$: 258, found: 258.

$[\alpha]^{25}_D$ = –80 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



Methyl (1*R*,9b*R*)-5,9b-dimethyl-4-oxo-2,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1-carboxylate (Table 3, entry 2). The title compound was prepared according to the General Procedure, using methyl (*E*)-3-(2-(*N*-methylbuta-2,3-dienamido)phenyl)but-2-enoate (122 mg, 0.45 mmol), (*S*)-**4** (27.0 mg, 0.045 mmol), and toluene (4.5 mL). After purification by column chromatography (eluted with 10% EtOAc in hexanes→50% EtOAc in hexanes), the title compound was isolated as a white solid (112 mg, 92% yield) with 90% ee.

HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 20% 2-propanol in hexanes; 1.0 mL/min; retention times: 6.3 min (major), 7.7 min (minor).

The second run was performed with (*R*)-**4**. The product was isolated as a white solid (109 mg, 89% yield) with 90% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, 1H, *J* = 7.8 Hz, *J* = 1.5 Hz), 7.30–7.27 (m, 1H), 7.13 (td, 1H, *J* = 7.6 Hz, *J* = 1.2 Hz), 7.01 (dd, 1H, *J* = 8.2 Hz, *J* = 1.1 Hz), 6.66 (dd, 1H, *J* = 3.3 Hz, *J* = 2.1 Hz),

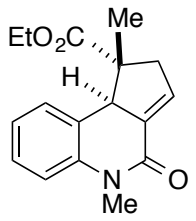
3.87 (s, 3H), 3.71 (t, 1H, J = 9.5 Hz), 3.42 (s, 3H), 3.18 (ddd, 1H, J = 18.6 Hz, J = 9.7 Hz, J = 2.1 Hz), 2.76 (ddd, 1H, J = 18.5 Hz, J = 8.9 Hz, J = 3.1 Hz), 1.25 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 161.8, 139.6, 138.5, 136.2, 135.0, 127.7, 126.1, 123.7, 115.0, 54.7, 52.2, 51.0, 34.7, 29.6, 24.0.

FT-IR (neat) 2952, 1732, 1661, 1599, 1447, 1355, 1277, 1204, 756 cm^{-1}.

LRMS (ESI) m/z $(M + H)^+$ calcd for $C_{16}H_{18}NO_3$: 272, found: 272.

$[\alpha]^{25}_D$ = +13 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



Methyl (1*R*,9b*R*)-1,5-dimethyl-4-oxo-2,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1-carboxylate (Table 3, entry 3). The title compound was prepared according to the General Procedure, using ethyl (*E*)-2-methyl-3-(2-(*N*-methylbuta-2,3-dienamido)phenyl)acrylate (22.8 mg, 0.08 mmol), (*S*)-**4** (9.6 mg, 0.016 mmol), and toluene (0.80 mL). After purification by column chromatography (eluted with 10% EtOAc in hexanes→50% EtOAc in hexanes), the title compound was isolated as a colorless oil (19 mg, 83% yield) with 82% ee.

HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 20% 2-propanol in hexanes; 1.0 mL/min; retention times: 5.8 min (major), 8.3 min (minor).

The second run was performed with (*R*)-**4**. The product was isolated as a white solid (18 mg, 80% yield) with 82% ee.

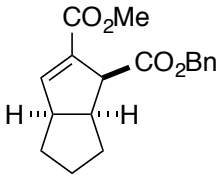
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.20 (m, 2H), 7.05–7.01 (m, 2H), 6.83 (td, 1H, J = 3.6 Hz, J = 2.1 Hz), 4.82 (s, 1H), 4.31 (qd, 2H, J = 6.8 Hz, J = 1.6 Hz), 3.41 (s, 3H), 3.06–3.01 (m, 1H), 2.55–2.51 (m, 1H), 1.35 (t, 3H, J = 6.9 Hz), 1.19 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 161.2, 140.2, 137.4, 133.8, 128.5, 127.7, 124.0, 122.6, 115.2, 61.4, 56.9, 49.7, 45.8, 29.4, 19.2, 14.4.

FT-IR (neat) 2979, 1729, 1645, 1456, 1360, 1273, 1211, 756 cm^{-1}.

LRMS (ESI) m/z $(M + H)^+$ calcd for $C_{17}H_{20}NO_3$: 286, found: 286.

$[\alpha]^{25}_D$ = +16 (c = 1.0, CH_2Cl_2; obtained with (*R*)-**4**).



1-Benzyl 2-methyl (1*S*,3a*R*,6a*S*)-1,3a,4,5,6,6a-hexahydropentalene-1,2-dicarboxylate (eq 9). The title compound was prepared according to the General Procedure, using 10-benzyl 1-methyl (*Z*)-deca-2,3,8-trienedioate (15.0 mg, 0.050 mmol), (*S*)-**4** (6.0 mg, 0.010 mmol), and toluene (0.50 mL). Reaction time: 48 h. The yield of the product was determined by ^{1}H NMR

analysis with the aid of an internal standard (61% yield). The title compound was isolated as a colorless oil by preparative TLC (eluted with 20% Et_2O in hexanes and then 20% acetone in hexanes). The ee of the product was determined by chiral HPLC (99% ee).

HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 3% 2-propanol in hexanes; 1.0 mL/min; retention times: 9.6 min (major), 14.0 min (minor).

The second run was performed with (*R*)-**4**. The yield of the product was determined by ^{1}H NMR analysis with the aid of an internal standard (63% yield). The ee of the product was determined by chiral HPLC (99% ee).

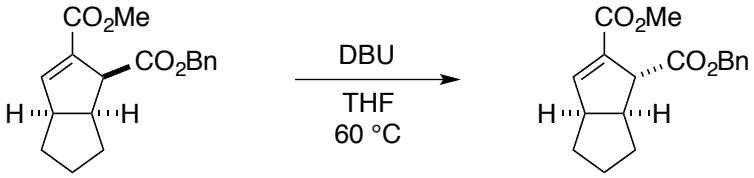
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38–7.29 (m, 5H), 6.71 (t, 1H, *J* = 2.3 Hz), 5.18 (d, 1H, *J* = 12.3 Hz), 5.12 (d, 1H, *J* = 12.3 Hz), 3.98 (dt, 1H, *J* = 10.0 Hz, *J* = 2.1 Hz), 3.64 (s, 3H), 3.34–3.28 (m, 1H), 3.11–3.04 (m, 1H), 1.82–1.73 (m, 1H), 1.61–1.49 (m, 3H), 1.48–1.40 (m, 1H), 1.39–1.32 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 165.0, 148.9, 136.0, 133.4, 128.6, 128.3, 66.4, 53.1, 51.6, 51.0, 47.8, 31.1, 30.2, 26.4.

FT-IR (neat) 2951, 1724, 1636, 1437, 1282, 1265, 1243, 1161, 1105, 1013 cm^{-1}.

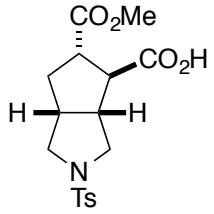
LRMS (ESI) *m*/*z* $(M + H)^+$ calcd for $C_{18}H_{21}O_4$: 301, found: 301.

$[\alpha]^{25}_D$ = +28 (c = 1.0, $CHCl_3$; obtained with (*S*)-**4**).



1-Benzyl 2-methyl (1*R*,3a*R*,6a*S*)-1,3a,4,5,6,6a-hexahydropentalene-1,2-dicarboxylate (derived from the product of eq 9). 1-Benzyl 2-methyl (1*S*,3a*R*,6a*S*)-1,3a,4,5,6,6a-hexahydropentalene-1,2-dicarboxylate (1.0 mg, 0.0033 mmol; 99% ee, obtained with (*S*)-**4**) and DBU (5.1 mg, 0.033 mmol) were dissolved in THF (0.30 mL), and the mixture was stirred at 60 °C for 6 h. It was then allowed to cool to r.t., the mixture was concentrated, and the residue was purified by preparative TLC. The absolute configuration of the product was determined by chiral HPLC analysis through comparison with authentic samples of known stereochemistry (Table 1, entry 1).

V. Stereoselective Derivatizations of Cycloaddition Products



(3a*R*,4*S*,5*S*,6a*R*)-5-(Methoxycarbonyl)-2-tosyloctahydrocyclopenta[*c*]pyrrole-4-carboxylic acid (eq 6). Palladium on carbon (10 wt% loading; 68.0 mg) was added to a 20-mL vial equipped with a stir bar. The vial was capped with a septum-lined cap, and then it was evacuated and back-filled with nitrogen (three cycles). Next, EtOAc (3.0 mL) was added via syringe, followed by a solution of 4-benzyl 5-methyl (3a*R*,4*S*,6a*R*)-2-tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole-4,5-dicarboxylate (68.3 mg, 0.15 mmol; 94% ee) in EtOAc (1.5 mL). While the reaction mixture was stirred at r.t., the vial was evacuated until the solvent just began to bubble, and then a hydrogen-filled balloon was attached to the vial. Next, the reaction mixture was stirred at r.t. for 12 h, and then it was filtered through a short pad of celite (eluted with EtOAc (1.0 mL)), and the filtrate was concentrated under reduced pressure, which afforded the title compound as a white solid. First run: 53 mg (97%). Second run: 54 mg (98%).

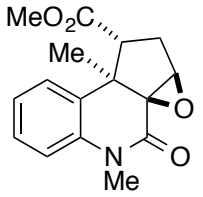
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, 2H, *J* = 8.2 Hz), 7.36–7.34 (m, 2H), 3.71 (s, 3H), 3.47–3.45 (m, 1H), 3.21–3.18 (m, 1H), 3.04–2.95 (m, 2H), 2.84–2.74 (m, 3H), 2.72–2.66 (m, 1H), 2.45 (s, 3H), 2.39–2.34 (m, 1H), 1.74–1.67 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 173.7, 144.0, 131.6, 129.8, 128.3, 53.8, 53.4, 53.0, 52.4, 48.4, 46.4, 41.5, 36.1, 21.7.

FT-IR (neat) 2954, 1733, 1344, 1164, 1027, 664 cm^{-1}.

LRMS (EI) *m*/*z* $(M + H)^+$ calcd for $C_{17}H_{22}NO_6S$: 368, found: 368.

$[\alpha]^{25}_D$ = +12 (c = 1.0, CH_2Cl_2).



Methyl (1*R*,2a*R*,3a*S*,9b*R*)-5,9b-dimethyl-4-oxo-1,2,2a,4,5,9b-hexahydrooxireno[2',3':1,5]cyclopenta[1,2-*c*]quinoline-1-carboxylate (eq 7). An oven-dried 20-mL vial was charged with MCPBA (360 mg, 1.60 mmol; based on 77% purity) and a stir bar. The vial was capped with a septum-lined cap, and then it was evacuated and back-filled with nitrogen (three cycles). Next, CH_2Cl_2 (anhydrous; 1.0 mL) was added via syringe, followed by a solution of methyl (1*R*,9b*R*)-5,9b-dimethyl-4-oxo-2,4,5,9b-tetrahydro-1H-cyclopenta[c]quinoline-1-carboxylate (54.3 mg, 0.20 mmol; 90% ee) in CH_2Cl_2 (1.0 mL). Grease was applied to the septum to seal the puncture holes, and then the reaction mixture was heated to 35 °C. After 16 h of stirring, the reaction mixture was allowed to cool to r.t., and then the reaction was quenched with a solution of sodium sulfite (saturated aqueous; 1.0 mL). The organic layer was separated,

and the aqueous layer was extracted with CH_2Cl_2 (2.0 mL x 3). The combined organic extracts were concentrated, and the residue was purified by column chromatography (eluted with 10% EtOAc in hexanes→40% EtOAc in hexanes), which furnished the title compound as a white crystalline solid. First run: 50 mg (88%). Second run: 47 mg (86%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, 1H, *J* = 7.5 Hz), 7.36–7.32 (m, 1H), 7.17–7.14 (m, 1H), 7.10 (d, 1H, *J* = 7.9 Hz), 4.22 (s, 1H), 3.82 (s, 3H), 3.45 (s, 3H), 3.13 (t, 1H, *J* = 7.9 Hz), 2.52–2.38 (m, 2H), 1.22 (s, 3H).

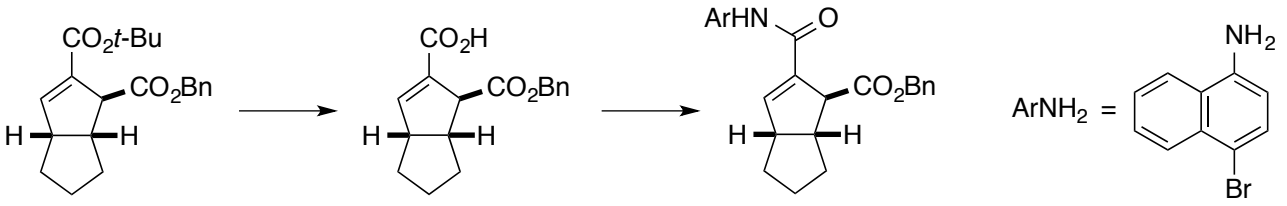
^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 164.0, 138.8, 132.2, 128.2, 126.7, 124.3, 116.0, 67.3, 58.4, 52.4, 44.6, 44.0, 30.8, 30.1, 18.9.

FT-IR (neat) 2954, 1728, 1694, 1455, 1360, 1238, 1024, 755 cm^{-1}.

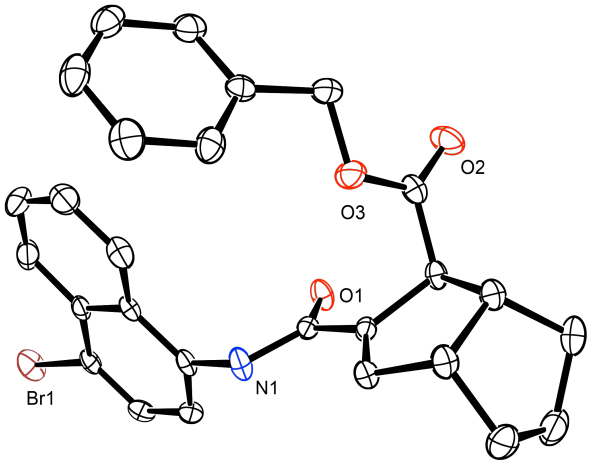
LRMS (EI) m/z $(M + H)^+$ calcd for $C_{16}H_{18}NO_4$: 288, found: 288.

$[\alpha]^{25}_D$ = –50 (c = 1.0, CH_2Cl_2).

VI. Determination of Stereochemistry by X-Ray Crystallography



Benzyl (1*S*,3a*S*,6a*R*)-2-((4-bromonaphthalen-1-yl)carbamoyl)-1,3a,4,5,6,6a-hexa hydropentalene-1-carboxylate (derived from the product of Table 1, entry 3). 1-Benzyl 2-(*tert*-butyl) (1*S*,3a*S*,6a*R*)-1,3a,4,5,6,6a-hexahydropentalene-1,2-dicarboxylate (17 mg, 0.050 mmol; 98% ee, obtained with (*S*)-**4**) was treated with TFA (0.5 mL), and this mixture was stirred at r.t. for 12 h. Next, toluene (2 mL) was added to the mixture, which was then concentrated under reduced pressure. The residue was added to a 4-mL vial, which was then capped, evacuated, and back-filled with nitrogen. CH_2Cl_2 (0.5 mL) and a drop of dimethylformamide were added in turn via syringe. The mixture was cooled to 0 °C, and then oxalyl chloride (5.0 μL) was added. The resulting mixture was stirred at r.t. for 1 h, and then Et_3N (11 μL) and 4-bromonaphthalen-1-amine (10 mg) were added. This mixture was stirred at r.t. for 16 h, and then it was concentrated under reduced pressure. The residue was purified by preparative TLC, which furnished the product as an off-white crystalline solid. X-ray quality crystals were grown from CH_2Cl_2/pentane.



A suitable crystal of $C_{27}H_{24}BrNO_3$ was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2,[1] the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[2] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.
2. Sheldrick, G. M. *Acta Crystallogr. A* **2008**, *64*, 112.

Table 1. Crystal data and structure refinement for a14003.

Identification code	a14003	
Empirical formula	$C_{27}H_{24}BrNO_3$	
Formula weight	490.38	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P\ 2_12_12_1$	
Unit cell dimensions	a = 9.6703(10) Å	α = 90°.
	b = 9.7969(10) Å	β = 90 °.
	c = 23.238(2) Å	γ = 90 °.
Volume	2201.5(4) $Å^3$	
Z	4	
Density (calculated)	1.480 Mg/m^3	
Absorption coefficient	1.897 mm^{-1}	
F(000)	1008	
Crystal size	0.2 x 0.12 x 0.1 mm^3	
Theta range for data collection	1.753 to 27.539°.	
Index ranges	-12<=h<=10, -12<=k<=12, -30<=l<=30	
Reflections collected	46998	
Independent reflections	5069 [R(int) = 0.0459]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6559	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5069 / 0 / 289	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0282, wR2 = 0.0652	
R indices (all data)	R1 = 0.0338, wR2 = 0.0668	
Absolute structure parameter (Flack)	0.012(3)	
Largest diff. peak and hole	0.684 and -0.273 $e/Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for a14003. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-701(1)	-8476(1)	-229(1)	32(1)
O(1)	-508(2)	-7325(2)	2600(1)	22(1)
O(2)	-2555(2)	-6488(2)	3925(1)	30(1)
O(3)	-2723(2)	-8665(2)	3637(1)	26(1)
N(1)	-68(3)	-9504(2)	2348(1)	21(1)
C(1)	-499(3)	-7848(2)	3809(1)	16(1)
C(2)	-59(3)	-8873(3)	3358(1)	15(1)
C(3)	430(3)	-10019(3)	3581(1)	17(1)
C(4)	484(3)	-9988(3)	4231(1)	20(1)
C(5)	-104(3)	-8556(3)	4392(1)	19(1)
C(6)	1058(3)	-7841(3)	4719(1)	26(1)
C(7)	2370(3)	-8507(4)	4493(1)	33(1)
C(8)	1980(3)	-10014(3)	4465(1)	30(1)
C(9)	-221(3)	-8502(3)	2738(1)	16(1)
C(10)	-2020(3)	-7548(3)	3795(1)	19(1)
C(11)	-4207(3)	-8580(3)	3660(1)	26(1)
C(12)	-4786(3)	-9764(3)	3330(1)	22(1)
C(13)	-4131(3)	-11024(3)	3321(1)	25(1)
C(14)	-4714(3)	-12115(3)	3040(1)	31(1)
C(15)	-5957(3)	-11963(3)	2749(1)	30(1)
C(16)	-6593(3)	-10714(3)	2745(1)	29(1)
C(17)	-6019(3)	-9611(3)	3035(1)	26(1)
C(18)	-244(3)	-9255(3)	1745(1)	17(1)
C(19)	841(3)	-8794(3)	1425(1)	21(1)
C(20)	680(3)	-8562(3)	830(1)	22(1)
C(21)	-562(3)	-8781(3)	579(1)	18(1)
C(22)	-1735(3)	-9242(3)	888(1)	18(1)
C(23)	-1546(3)	-9510(3)	1490(1)	17(1)
C(24)	-2676(3)	-10035(3)	1808(1)	25(1)
C(25)	-3926(3)	-10247(3)	1552(1)	31(1)
C(26)	-4111(3)	-9957(3)	963(1)	32(1)
C(27)	-3045(3)	-9469(3)	643(1)	27(1)

Table 3. Bond lengths [Å] and angles [°] for a14003.

Br(1)-C(21)	1.907(2)
O(1)-C(9)	1.229(3)
O(2)-C(10)	1.199(3)
O(3)-C(10)	1.339(3)
O(3)-C(11)	1.438(3)
N(1)-C(9)	1.345(3)
N(1)-C(18)	1.433(3)
C(1)-C(2)	1.513(3)
C(1)-C(5)	1.569(3)
C(1)-C(10)	1.501(4)
C(2)-C(3)	1.325(4)
C(2)-C(9)	1.493(3)
C(3)-C(4)	1.510(3)
C(4)-C(5)	1.559(4)
C(4)-C(8)	1.546(4)
C(5)-C(6)	1.528(4)
C(6)-C(7)	1.521(4)
C(7)-C(8)	1.525(5)
C(11)-C(12)	1.500(4)
C(12)-C(13)	1.387(4)
C(12)-C(17)	1.383(4)
C(13)-C(14)	1.374(4)
C(14)-C(15)	1.387(5)
C(15)-C(16)	1.370(5)
C(16)-C(17)	1.389(4)
C(18)-C(19)	1.362(4)
C(18)-C(23)	1.413(4)
C(19)-C(20)	1.409(3)
C(20)-C(21)	1.352(4)
C(21)-C(22)	1.416(4)
C(22)-C(23)	1.437(3)
C(22)-C(27)	1.407(4)
C(23)-C(24)	1.415(4)
C(24)-C(25)	1.362(4)
C(25)-C(26)	1.410(4)
C(26)-C(27)	1.358(4)

C(10)-O(3)-C(11)	116.6(2)
C(9)-N(1)-C(18)	121.5(2)
C(2)-C(1)-C(5)	103.7(2)
C(10)-C(1)-C(2)	113.0(2)
C(10)-C(1)-C(5)	110.1(2)
C(3)-C(2)-C(1)	113.0(2)
C(3)-C(2)-C(9)	128.5(2)
C(9)-C(2)-C(1)	118.5(2)
C(2)-C(3)-C(4)	112.8(2)

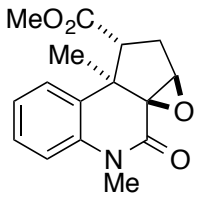
C(3)-C(4)-C(5)	104.2(2)
C(3)-C(4)-C(8)	112.5(2)
C(8)-C(4)-C(5)	105.8(2)
C(4)-C(5)-C(1)	106.18(19)
C(6)-C(5)-C(1)	113.9(2)
C(6)-C(5)-C(4)	105.3(2)
C(7)-C(6)-C(5)	104.2(2)
C(6)-C(7)-C(8)	102.9(2)
C(7)-C(8)-C(4)	103.3(2)
O(1)-C(9)-N(1)	122.2(2)
O(1)-C(9)-C(2)	120.3(2)
N(1)-C(9)-C(2)	117.5(2)
O(2)-C(10)-O(3)	123.9(3)
O(2)-C(10)-C(1)	125.9(2)
O(3)-C(10)-C(1)	110.1(2)
O(3)-C(11)-C(12)	107.9(2)
C(13)-C(12)-C(11)	121.7(3)
C(17)-C(12)-C(11)	119.4(3)
C(17)-C(12)-C(13)	118.9(3)
C(14)-C(13)-C(12)	120.8(3)
C(13)-C(14)-C(15)	120.3(3)
C(16)-C(15)-C(14)	119.2(3)
C(15)-C(16)-C(17)	120.8(3)
C(12)-C(17)-C(16)	120.0(3)
C(19)-C(18)-N(1)	119.9(2)
C(19)-C(18)-C(23)	121.1(2)
C(23)-C(18)-N(1)	119.0(2)
C(18)-C(19)-C(20)	120.2(3)
C(21)-C(20)-C(19)	119.7(2)
C(20)-C(21)-Br(1)	117.60(19)
C(20)-C(21)-C(22)	122.9(2)
C(22)-C(21)-Br(1)	119.5(2)
C(21)-C(22)-C(23)	116.8(2)
C(27)-C(22)-C(21)	124.6(2)
C(27)-C(22)-C(23)	118.6(3)
C(18)-C(23)-C(22)	119.2(2)
C(18)-C(23)-C(24)	122.3(2)
C(24)-C(23)-C(22)	118.4(3)
C(25)-C(24)-C(23)	120.9(3)
C(24)-C(25)-C(26)	120.3(3)
C(27)-C(26)-C(25)	120.4(3)
C(26)-C(27)-C(22)	121.2(3)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for a14003. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

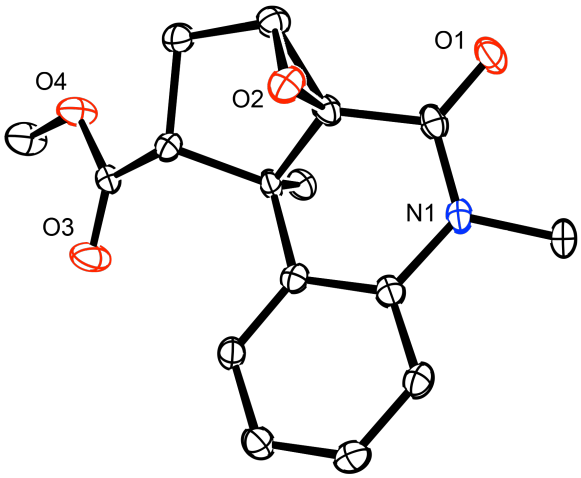
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	47(1)	35(1)	13(1)	3(1)	3(1)	7(1)
O(1)	36(1)	14(1)	16(1)	0(1)	-2(1)	3(1)
O(2)	29(1)	20(1)	41(1)	-9(1)	8(1)	2(1)
O(3)	19(1)	21(1)	38(1)	-6(1)	-1(1)	0(1)
N(1)	38(1)	12(1)	13(1)	1(1)	-5(1)	6(1)
C(1)	23(2)	11(1)	15(1)	-1(1)	0(1)	-2(1)
C(2)	14(1)	16(1)	14(1)	-1(1)	-1(1)	-2(1)
C(3)	21(2)	16(1)	15(1)	-2(1)	0(1)	0(1)
C(4)	26(2)	17(1)	15(1)	2(1)	-1(1)	-1(1)
C(5)	24(1)	18(1)	14(1)	2(1)	1(1)	-2(1)
C(6)	35(2)	25(1)	17(1)	0(1)	-5(1)	-7(1)
C(7)	25(2)	51(2)	22(1)	-2(2)	-5(1)	-7(2)
C(8)	29(2)	42(2)	20(1)	3(1)	-7(1)	8(2)
C(9)	15(1)	16(1)	16(1)	-1(1)	-2(1)	0(1)
C(10)	26(2)	16(1)	14(1)	1(1)	3(1)	-1(1)
C(11)	18(1)	27(1)	34(1)	-7(1)	0(1)	5(1)
C(12)	19(1)	26(2)	20(1)	-1(1)	6(1)	-2(1)
C(13)	28(2)	29(1)	18(1)	1(1)	-3(1)	-3(1)
C(14)	38(2)	25(2)	30(2)	2(1)	0(1)	-3(1)
C(15)	35(2)	30(2)	25(1)	0(1)	0(1)	-16(1)
C(16)	22(2)	42(2)	22(1)	2(1)	0(1)	-6(1)
C(17)	21(2)	30(2)	26(1)	0(1)	4(1)	1(1)
C(18)	27(2)	12(1)	13(1)	-2(1)	0(1)	3(1)
C(19)	19(1)	19(1)	24(1)	-2(1)	-1(1)	4(1)
C(20)	21(1)	23(1)	21(1)	0(1)	8(1)	3(2)
C(21)	28(2)	18(1)	10(1)	-1(1)	2(1)	4(1)
C(22)	23(2)	14(1)	17(1)	-5(1)	-2(1)	3(1)
C(23)	24(2)	12(1)	16(1)	-3(1)	3(1)	2(1)
C(24)	33(2)	20(1)	21(1)	-2(1)	6(1)	-4(1)
C(25)	28(2)	28(2)	38(2)	-8(1)	12(1)	-10(1)
C(26)	22(2)	31(2)	44(2)	-10(1)	-6(1)	-6(1)
C(27)	31(2)	24(1)	26(1)	-7(1)	-7(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal_05.

	x	y	z	U(eq)
H(1)	146	-10332	2465	25
H(1A)	39	-6983	3763	20
H(3)	717	-10779	3357	21
H(4)	-86	-10737	4402	24
H(5)	-939	-8654	4643	22
H(6A)	1058	-6848	4640	31
H(6B)	964	-7985	5139	31
H(7A)	3157	-8355	4758	39
H(7B)	2614	-8151	4107	39
H(8A)	2017	-10439	4851	36
H(8B)	2602	-10519	4202	36
H(11A)	-4524	-7710	3489	32
H(11B)	-4525	-8615	4065	32
H(13)	-3268	-11133	3512	30
H(14)	-4265	-12977	3046	37
H(15)	-6362	-12716	2555	36
H(16)	-7437	-10600	2541	35
H(17)	-6473	-8751	3031	31
H(19)	1708	-8628	1604	25
H(20)	1440	-8253	607	26
H(24)	-2562	-10243	2204	30
H(25)	-4676	-10591	1773	38
H(26)	-4988	-10104	789	39
H(27)	-3187	-9277	247	32



Methyl (1*R*,2a*R*,3a*S*,9b*R*)-5,9b-dimethyl-4-oxo-1,2,2a,4,5,9b-hexahydrooxireno[2',3':1,5]cyclopenta[1,2-*c*]quinoline-1-carboxylate (eq 7; derived from the product of Table 3, entry 2 obtained with (*S*)-**4**). X-ray quality crystals were obtained by slowly evaporating EtOAc from a saturated solution at r.t.



A crystal of $C_{16}H_{17}NO_4$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. The crystal was determined to be a two-component non-merohedral twin. Both components were integrated and the data processed with TWINABS. Using Olex2,[1] the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[2] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.
2. Sheldrick, G. M. *Acta Crystallogr. A* **2008**, *64*, 112.

Table 6. Crystal data and structure refinement for crystal_03.

Identification code	crystal_03	
Empirical formula	$C_{16}H_{17}NO_4$	
Formula weight	287.30	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.8954(3) Å	α = 90°.
	b = 7.4269(4) Å	β = 90°
	c = 54.090(2) Å	γ = 90°
Volume	2770.1(2) $Å^3$	
Z	8	
Density (calculated)	1.378 Mg/m^3	
Absorption coefficient	0.820 mm^{-1}	
F(000)	1216	
Crystal size	0.6 x 0.35 x 0.16 mm^3	
Theta range for data collection	3.268 to 68.533°.	
Reflections collected	134537	
Independent reflections	5087	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.753056 and 0.614834	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5087 / 0 / 385	
Goodness-of-fit on F^2	1.112	
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0728	
R indices (all data)	R1 = 0.0307, wR2 = 0.0730	
Absolute structure parameter	0.06(3)	
Largest diff. peak and hole	0.141 and -0.230 $e/Å^{-3}$	

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal_03. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8287(2)	5943(2)	7555(1)	22(1)
O(2)	7026(2)	7510(2)	7036(1)	20(1)
O(3)	11338(3)	4971(2)	6387(1)	33(1)
O(4)	12833(2)	7416(2)	6527(1)	24(1)
N(1)	7266(3)	3678(2)	7300(1)	17(1)
C(1)	8066(3)	5319(3)	7347(1)	16(1)
C(2)	8575(3)	6309(3)	7116(1)	16(1)
C(3)	8956(3)	8224(3)	7087(1)	19(1)
C(4)	10108(3)	8483(3)	6854(1)	19(1)
C(5)	9782(3)	6717(3)	6706(1)	16(1)
C(6)	9451(3)	5224(3)	6908(1)	14(1)
C(7)	11391(3)	4392(3)	6992(1)	18(1)
C(8)	7995(3)	3756(3)	6852(1)	14(1)
C(9)	6947(3)	3030(3)	7053(1)	16(1)
C(10)	5608(3)	1665(3)	7014(1)	18(1)
C(11)	5314(3)	981(3)	6777(1)	20(1)
C(12)	6343(3)	1669(3)	6579(1)	20(1)
C(13)	7661(3)	3061(3)	6617(1)	17(1)
C(14)	11372(3)	6246(3)	6524(1)	17(1)
C(15)	14431(3)	6997(3)	6362(1)	28(1)
C(16)	6588(3)	2601(3)	7509(1)	24(1)
O(5)	9573(2)	5743(2)	4936(1)	22(1)
O(6)	11545(2)	4555(2)	5437(1)	19(1)
O(7)	8726(2)	8202(2)	6122(1)	31(1)
O(8)	11244(2)	9742(2)	5980(1)	31(1)
N(2)	7307(2)	4588(2)	5200(1)	17(1)
C(17)	8999(3)	5442(3)	5147(1)	16(1)
C(18)	10117(3)	5926(3)	5374(1)	15(1)
C(19)	12161(3)	6401(3)	5394(1)	18(1)
C(20)	12438(3)	7409(3)	5632(1)	19(1)
C(21)	10611(3)	6943(3)	5788(1)	16(1)
C(22)	8964(3)	6590(3)	5594(1)	14(1)
C(23)	7921(3)	8352(3)	5523(1)	18(1)
C(24)	7522(3)	5111(3)	5651(1)	14(1)
C(25)	6760(3)	4133(3)	5448(1)	15(1)
C(26)	5475(3)	2734(3)	5490(1)	18(1)
C(27)	4877(3)	2332(3)	5728(1)	21(1)
C(28)	5576(3)	3307(3)	5927(1)	21(1)
C(29)	6918(3)	4671(3)	5887(1)	17(1)
C(30)	10062(3)	8336(3)	5981(1)	16(1)
C(31)	10769(4)	11163(3)	6156(1)	39(1)
C(32)	6088(3)	3998(3)	4993(1)	23(1)

Table 8. Bond lengths [Å] and angles [°] for crystal_03.

O(1)-C(1)	1.225(2)
O(2)-C(2)	1.457(2)
O(2)-C(3)	1.459(3)
O(3)-C(14)	1.201(3)
O(4)-C(14)	1.330(3)
O(4)-C(15)	1.450(3)
N(1)-C(1)	1.362(3)
N(1)-C(9)	1.434(2)
N(1)-C(16)	1.466(3)
C(1)-C(2)	1.493(3)
C(2)-C(3)	1.455(3)
C(2)-C(6)	1.511(3)
C(3)-H(3)	1.0000
C(3)-C(4)	1.503(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(5)	1.553(3)
C(5)-H(5)	1.0000
C(5)-C(6)	1.572(3)
C(5)-C(14)	1.515(3)
C(6)-C(7)	1.544(3)
C(6)-C(8)	1.513(3)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(9)	1.414(3)
C(8)-C(13)	1.388(3)
C(9)-C(10)	1.388(3)
C(10)-H(10)	0.9500
C(10)-C(11)	1.390(3)
C(11)-H(11)	0.9500
C(11)-C(12)	1.384(3)
C(12)-H(12)	0.9500
C(12)-C(13)	1.392(3)
C(13)-H(13)	0.9500
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
O(5)-C(17)	1.225(2)
O(6)-C(18)	1.457(2)
O(6)-C(19)	1.454(3)
O(7)-C(30)	1.200(3)
O(8)-C(30)	1.325(3)

O(8)-C(31)	1.456(3)
N(2)-C(17)	1.360(3)
N(2)-C(25)	1.434(3)
N(2)-C(32)	1.467(3)
C(17)-C(18)	1.495(3)
C(18)-C(19)	1.457(3)
C(18)-C(22)	1.513(3)
C(19)-H(19)	1.0000
C(19)-C(20)	1.504(3)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(20)-C(21)	1.554(3)
C(21)-H(21)	1.0000
C(21)-C(22)	1.569(3)
C(21)-C(30)	1.516(3)
C(22)-C(23)	1.541(3)
C(22)-C(24)	1.513(3)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-C(25)	1.414(3)
C(24)-C(29)	1.386(3)
C(25)-C(26)	1.384(3)
C(26)-H(26)	0.9500
C(26)-C(27)	1.389(3)
C(27)-H(27)	0.9500
C(27)-C(28)	1.383(3)
C(28)-H(28)	0.9500
C(28)-C(29)	1.389(3)
C(29)-H(29)	0.9500
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800

C(2)-O(2)-C(3)	59.86(13)
C(14)-O(4)-C(15)	115.38(16)
C(1)-N(1)-C(9)	122.63(16)
C(1)-N(1)-C(16)	118.04(16)
C(9)-N(1)-C(16)	119.19(17)
O(1)-C(1)-N(1)	124.27(18)
O(1)-C(1)-C(2)	123.61(19)
N(1)-C(1)-C(2)	112.08(17)
O(2)-C(2)-C(1)	112.17(16)
O(2)-C(2)-C(6)	113.52(16)
C(1)-C(2)-C(6)	117.16(17)

C(3)-C(2)-O(2)	60.13(13)
C(3)-C(2)-C(1)	127.77(18)
C(3)-C(2)-C(6)	111.73(17)
O(2)-C(3)-H(3)	120.7
O(2)-C(3)-C(4)	111.68(17)
C(2)-C(3)-O(2)	60.01(13)
C(2)-C(3)-H(3)	120.7
C(2)-C(3)-C(4)	108.03(17)
C(4)-C(3)-H(3)	120.7
C(3)-C(4)-H(4A)	110.9
C(3)-C(4)-H(4B)	110.9
C(3)-C(4)-C(5)	104.38(17)
H(4A)-C(4)-H(4B)	108.9
C(5)-C(4)-H(4A)	110.9
C(5)-C(4)-H(4B)	110.9
C(4)-C(5)-H(5)	107.7
C(4)-C(5)-C(6)	104.99(15)
C(6)-C(5)-H(5)	107.7
C(14)-C(5)-C(4)	115.20(17)
C(14)-C(5)-H(5)	107.7
C(14)-C(5)-C(6)	113.19(17)
C(2)-C(6)-C(5)	101.49(16)
C(2)-C(6)-C(7)	109.79(16)
C(2)-C(6)-C(8)	105.54(16)
C(7)-C(6)-C(5)	111.26(16)
C(8)-C(6)-C(5)	117.79(16)
C(8)-C(6)-C(7)	110.25(16)
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(6)	117.39(17)
C(13)-C(8)-C(6)	124.10(18)
C(13)-C(8)-C(9)	118.49(19)
C(8)-C(9)-N(1)	120.63(18)
C(10)-C(9)-N(1)	119.37(18)
C(10)-C(9)-C(8)	120.00(18)
C(9)-C(10)-H(10)	119.8
C(9)-C(10)-C(11)	120.38(19)
C(11)-C(10)-H(10)	119.8
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-C(10)	120.2(2)
C(12)-C(11)-H(11)	119.9
C(11)-C(12)-H(12)	120.2
C(11)-C(12)-C(13)	119.57(19)
C(13)-C(12)-H(12)	120.2

C(8)-C(13)-C(12)	121.37(19)
C(8)-C(13)-H(13)	119.3
C(12)-C(13)-H(13)	119.3
O(3)-C(14)-O(4)	122.48(19)
O(3)-C(14)-C(5)	124.57(19)
O(4)-C(14)-C(5)	112.95(16)
O(4)-C(15)-H(15A)	109.5
O(4)-C(15)-H(15B)	109.5
O(4)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
N(1)-C(16)-H(16A)	109.5
N(1)-C(16)-H(16B)	109.5
N(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(19)-O(6)-C(18)	60.08(13)
C(30)-O(8)-C(31)	115.60(17)
C(17)-N(2)-C(25)	122.38(16)
C(17)-N(2)-C(32)	117.91(16)
C(25)-N(2)-C(32)	119.54(17)
O(5)-C(17)-N(2)	124.11(19)
O(5)-C(17)-C(18)	123.60(19)
N(2)-C(17)-C(18)	112.27(16)
O(6)-C(18)-C(17)	111.86(16)
O(6)-C(18)-C(19)	59.85(13)
O(6)-C(18)-C(22)	113.58(16)
C(17)-C(18)-C(22)	116.97(17)
C(19)-C(18)-C(17)	128.18(18)
C(19)-C(18)-C(22)	111.79(17)
O(6)-C(19)-C(18)	60.07(13)
O(6)-C(19)-H(19)	120.7
O(6)-C(19)-C(20)	111.73(17)
C(18)-C(19)-H(19)	120.7
C(18)-C(19)-C(20)	107.86(17)
C(20)-C(19)-H(19)	120.7
C(19)-C(20)-H(20A)	110.8
C(19)-C(20)-H(20B)	110.8
C(19)-C(20)-C(21)	104.51(16)
H(20A)-C(20)-H(20B)	108.9
C(21)-C(20)-H(20A)	110.8
C(21)-C(20)-H(20B)	110.8
C(20)-C(21)-H(21)	107.7
C(20)-C(21)-C(22)	105.17(15)
C(22)-C(21)-H(21)	107.7
C(30)-C(21)-C(20)	114.99(17)

C(30)-C(21)-H(21)	107.7
C(30)-C(21)-C(22)	113.17(16)
C(18)-C(22)-C(21)	101.55(15)
C(18)-C(22)-C(23)	109.12(16)
C(18)-C(22)-C(24)	105.54(16)
C(23)-C(22)-C(21)	111.19(16)
C(24)-C(22)-C(21)	117.45(16)
C(24)-C(22)-C(23)	111.14(16)
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(25)-C(24)-C(22)	117.41(17)
C(29)-C(24)-C(22)	123.77(17)
C(29)-C(24)-C(25)	118.82(19)
C(24)-C(25)-N(2)	120.30(18)
C(26)-C(25)-N(2)	119.73(18)
C(26)-C(25)-C(24)	119.96(18)
C(25)-C(26)-H(26)	120.0
C(25)-C(26)-C(27)	120.07(19)
C(27)-C(26)-H(26)	120.0
C(26)-C(27)-H(27)	119.8
C(28)-C(27)-C(26)	120.5(2)
C(28)-C(27)-H(27)	119.8
C(27)-C(28)-H(28)	120.2
C(27)-C(28)-C(29)	119.59(19)
C(29)-C(28)-H(28)	120.2
C(24)-C(29)-C(28)	121.01(19)
C(24)-C(29)-H(29)	119.5
C(28)-C(29)-H(29)	119.5
O(7)-C(30)-O(8)	122.57(19)
O(7)-C(30)-C(21)	124.90(19)
O(8)-C(30)-C(21)	112.52(16)
O(8)-C(31)-H(31A)	109.5
O(8)-C(31)-H(31B)	109.5
O(8)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
N(2)-C(32)-H(32A)	109.5
N(2)-C(32)-H(32B)	109.5
N(2)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5

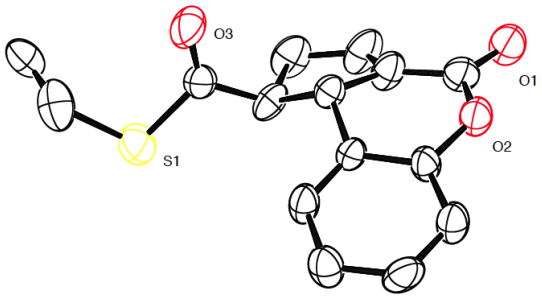
Table 9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal_03. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	28(1)	25(1)	13(1)	-3(1)	3(1)	2(1)
O(2)	18(1)	18(1)	24(1)	1(1)	2(1)	3(1)
O(3)	39(1)	33(1)	28(1)	-15(1)	17(1)	-16(1)
O(4)	18(1)	26(1)	29(1)	-11(1)	8(1)	-5(1)
N(1)	19(1)	19(1)	12(1)	2(1)	2(1)	0(1)
C(1)	15(1)	21(1)	13(1)	0(1)	3(1)	3(1)
C(2)	16(1)	16(1)	14(1)	-1(1)	1(1)	4(1)
C(3)	18(1)	18(1)	20(1)	-2(1)	2(1)	1(1)
C(4)	23(1)	16(1)	19(1)	-1(1)	3(1)	-1(1)
C(5)	17(1)	15(1)	16(1)	2(1)	1(1)	-3(1)
C(6)	16(1)	17(1)	9(1)	0(1)	2(1)	0(1)
C(7)	17(1)	20(1)	16(1)	-1(1)	1(1)	3(1)
C(8)	14(1)	13(1)	16(1)	1(1)	1(1)	2(1)
C(9)	17(1)	15(1)	15(1)	0(1)	1(1)	4(1)
C(10)	18(1)	18(1)	19(1)	3(1)	4(1)	0(1)
C(11)	19(1)	17(1)	24(1)	0(1)	-1(1)	-3(1)
C(12)	24(1)	21(1)	16(1)	-1(1)	-3(1)	0(1)
C(13)	21(1)	17(1)	14(1)	2(1)	1(1)	0(1)
C(14)	21(1)	18(1)	11(1)	1(1)	-1(1)	-2(1)
C(15)	20(1)	32(1)	33(1)	-10(1)	10(1)	-4(1)
C(16)	33(1)	24(1)	14(1)	4(1)	5(1)	-5(1)
O(5)	25(1)	28(1)	13(1)	-1(1)	4(1)	1(1)
O(6)	16(1)	19(1)	22(1)	-2(1)	-1(1)	4(1)
O(7)	34(1)	33(1)	27(1)	-13(1)	16(1)	-14(1)
O(8)	30(1)	25(1)	38(1)	-16(1)	18(1)	-11(1)
N(2)	18(1)	21(1)	12(1)	-3(1)	-2(1)	-1(1)
C(17)	20(1)	15(1)	14(1)	-2(1)	0(1)	4(1)
C(18)	16(1)	14(1)	15(1)	-1(1)	1(1)	2(1)
C(19)	16(1)	19(1)	19(1)	-3(1)	3(1)	0(1)
C(20)	15(1)	24(1)	18(1)	-3(1)	3(1)	-3(1)
C(21)	14(1)	18(1)	15(1)	-1(1)	0(1)	-2(1)
C(22)	16(1)	16(1)	10(1)	0(1)	1(1)	1(1)
C(23)	20(1)	17(1)	16(1)	0(1)	1(1)	2(1)
C(24)	11(1)	16(1)	14(1)	-1(1)	-1(1)	3(1)
C(25)	14(1)	16(1)	15(1)	-1(1)	-1(1)	4(1)
C(26)	16(1)	18(1)	22(1)	-5(1)	-3(1)	1(1)
C(27)	19(1)	18(1)	26(1)	1(1)	2(1)	-5(1)
C(28)	21(1)	24(1)	17(1)	3(1)	2(1)	-1(1)
C(29)	16(1)	18(1)	16(1)	0(1)	-1(1)	-1(1)
C(30)	16(1)	20(1)	11(1)	1(1)	-2(1)	-2(1)
C(31)	40(1)	30(1)	46(2)	-24(1)	21(1)	-14(1)
C(32)	23(1)	32(1)	16(1)	-6(1)	-4(1)	-3(1)

Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal_03.

	x	y	z	U(eq)
H(3)	9192	9003	7235	23
H(4A)	11501	8656	6892	23
H(4B)	9633	9539	6761	23
H(5)	8547	6852	6611	19
H(7A)	11175	3661	7141	27
H(7B)	12316	5355	7030	27
H(7C)	11914	3630	6860	27
H(10)	4887	1196	7149	22
H(11)	4404	38	6752	24
H(12)	6151	1194	6418	25
H(13)	8346	3546	6480	21
H(15A)	14979	5823	6407	43
H(15B)	15434	7925	6378	43
H(15C)	13962	6958	6191	43
H(16A)	7159	3067	7662	36
H(16B)	6980	1344	7486	36
H(16C)	5171	2671	7520	36
H(19)	12930	6724	5244	22
H(20A)	12521	8722	5602	23
H(20B)	13633	7010	5718	23
H(21)	10870	5784	5876	19
H(23A)	7069	8134	5381	27
H(23B)	8885	9269	5480	27
H(23C)	7148	8774	5664	27
H(26)	5001	2047	5354	22
H(27)	3982	1380	5756	25
H(28)	5140	3046	6090	25
H(29)	7431	5313	6025	20
H(31A)	10912	10705	6325	58
H(31B)	9428	11556	6129	58
H(31C)	11648	12184	6131	58
H(32A)	6361	2732	4956	35
H(32B)	6371	4736	4848	35
H(32C)	4719	4133	5038	35

***S*-Ethyl (1*S*,9b*S*)-4-oxo-1,2,4,9b-tetrahydrocyclopenta[*c*]chromene-1-carbothioate** (eq 5; obtained with (*R*)-**3**). X-ray quality crystals were grown from CH_2Cl_2/pentane.



A crystal of $C_{15}H_{14}O_3S$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Apex-II diffractometer with filtered Mo-Kα radiation at a temperature of 200 K. Using Olex2,[1] the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[2] refinement package using Least Squares minimization. Disorder in the thioester functional group was modeled using similarity restraints placed on appropriate atoms and atom pairs. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.
2. Sheldrick, G. M. *Acta Crystallogr. A* **2008**, *64*, 112.

Table 11. Crystal data and structure refinement for crystal_04.

Identification code	crystal_04	
Empirical formula	$C_{15}H_{14}O_3S$	
Formula weight	274.32	
Temperature	200 K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	$P3_1$	
Unit cell dimensions	a = 20.0103(6) Å	α = 90°
	b = 20.0103(6) Å	β = 90°
	c = 11.7669(4) Å	γ = 120°
Volume	4080.4(3) $Å^3$	
Z	12	
Density (calculated)	1.340 Mg/m^3	
Absorption coefficient	0.238 mm^{-1}	
F(000)	1728	
Crystal size	0.34 x 0.24 x 0.22 mm^3	
Theta range for data collection	1.175 to 25.679°.	
Index ranges	-24<=h<=24, -24<=k<=24, -14<=l<=14	
Reflections collected	50935	
Independent reflections	10371 [R(int) = 0.0267]	
Completeness to theta = 26.000°	97.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7471 and 0.6876	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10371 / 194 / 762	
Goodness-of-fit on F^2	1.090	
Final R indices [I>2sigma(I)]	R1 = 0.0878, wR2 = 0.2299	
R indices (all data)	R1 = 0.0917, wR2 = 0.2332	
Absolute structure parameter	0.113(12)	
Largest diff. peak and hole	0.518 and -0.480 $e/Å^{-3}$	

Table 12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for crystal_04. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	-6958(2)	-4465(2)	-2705(2)	63(1)
O(1)	-10971(4)	-7643(4)	-3970(8)	66(2)
O(2)	-9998(3)	-7867(3)	-3953(6)	47(1)
O(3)	-7711(5)	-4709(4)	-4613(6)	72(2)
C(1)	-10289(5)	-7385(6)	-3844(8)	48(2)
C(2)	-9243(5)	-7662(4)	-3666(7)	38(2)
C(3)	-9092(5)	-8257(5)	-3486(8)	45(2)
C(4)	-8355(5)	-8090(5)	-3209(9)	50(2)
C(5)	-7759(5)	-7323(5)	-3090(9)	47(2)
C(6)	-7940(5)	-6737(5)	-3293(8)	42(2)
C(7)	-8660(5)	-6880(4)	-3570(7)	37(2)
C(8)	-8861(5)	-6272(4)	-3821(7)	36(2)
C(9)	-9711(5)	-6576(5)	-3592(9)	50(2)
C(10)	-9815(7)	-6023(6)	-3179(11)	68(3)
C(11)	-9103(7)	-5280(6)	-2993(11)	63(3)
C(12)	-8472(6)	-5524(5)	-3100(8)	46(2)
C(13)	-7748(5)	-4894(5)	-3640(8)	44(2)
C(14)	-6189(7)	-3751(7)	-3612(11)	69(3)
C(15)	-6186(6)	-3019(7)	-3680(10)	64(3)
S(1B)	-7113(7)	-9103(6)	-2879(10)	55(3)
S(1E)	-6923(8)	-9285(9)	-2922(11)	85(4)
O(1B)	-10927(4)	-12648(5)	-3690(10)	87(3)
O(2B)	-9961(3)	-12871(3)	-3694(6)	51(2)
O(3B)	-7455(18)	-9919(17)	-4700(20)	90(9)
O(3E)	-7752(16)	-9740(16)	-4760(17)	97(9)
C(1B)	-10234(6)	-12366(6)	-3607(11)	65(3)
C(2B)	-9181(5)	-12626(5)	-3485(8)	46(2)
C(3B)	-9045(6)	-13235(5)	-3258(8)	53(2)
C(4B)	-8282(7)	-13046(7)	-3078(9)	61(3)
C(5B)	-7701(6)	-12292(7)	-3096(10)	62(3)
C(6B)	-7845(6)	-11695(6)	-3314(8)	53(2)
C(7B)	-8602(5)	-11859(5)	-3488(8)	45(2)
C(8B)	-8833(5)	-11262(5)	-3757(9)	48(2)
C(9B)	-9669(6)	-11555(6)	-3494(10)	59(3)
C(10B)	-9776(7)	-11017(7)	-3027(12)	78(4)
C(11B)	-9042(8)	-10266(7)	-2960(14)	83(4)
C(12B)	-8417(6)	-10507(5)	-3120(9)	51(2)
C(13B)	-7691(7)	-9873(6)	-3749(9)	63(3)
C(14B)	-6230(16)	-8565(17)	-3820(30)	67(6)
C(14E)	-6435(19)	-8472(16)	-3980(20)	84(9)
C(15B)	-6350(20)	-7910(20)	-3940(40)	90(9)
C(15E)	-5924(15)	-7762(13)	-3400(30)	84(7)
S(1A)	-4649(3)	-5677(6)	-3716(3)	72(2)

S(1D)	-4405(19)	-5200(20)	-3620(30)	85(6)
O(1A)	-688(4)	-5021(4)	-2614(7)	62(2)
O(2A)	-1644(3)	-6213(3)	-2548(5)	42(1)
O(3A)	-4020(5)	-5503(8)	-1753(6)	103(4)
C(1A)	-1367(5)	-5438(5)	-2689(8)	42(2)
C(2A)	-2418(4)	-6749(4)	-2806(6)	32(2)
C(3A)	-2562(5)	-7498(5)	-2984(8)	42(2)
C(4A)	-3322(6)	-8063(5)	-3173(8)	49(2)
C(5A)	-3895(5)	-7905(5)	-3230(8)	49(2)
C(6A)	-3756(5)	-7152(5)	-3053(7)	42(2)
C(7A)	-2987(4)	-6553(4)	-2823(6)	30(2)
C(8A)	-2785(4)	-5736(5)	-2599(7)	35(2)
C(9A)	-1939(5)	-5198(5)	-2868(7)	39(2)
C(10A)	-1815(6)	-4547(6)	-3285(10)	56(3)
C(11A)	-2589(7)	-4535(6)	-3342(9)	58(3)
C(12A)	-3181(5)	-5380(5)	-3302(8)	42(2)
C(13A)	-3917(5)	-5504(6)	-2736(8)	46(2)
C(14A)	-5415(10)	-5734(14)	-2784(18)	80(5)
C(14D)	-5260(50)	-5740(50)	-2700(80)	84(11)
C(15A)	-5305(12)	-4973(13)	-2500(20)	102(6)
C(15D)	-5260(50)	-5230(60)	-1820(80)	102(14)
S(1C)	-9640(30)	-4121(16)	-450(20)	77(8)
S(1F)	-9218(11)	-3930(6)	-379(5)	68(3)
O(1C)	-9984(5)	-662(6)	366(12)	108(4)
O(2C)	-8806(4)	-452(4)	390(7)	58(2)
O(3C)	-9877(8)	-3631(6)	1333(8)	110(4)
C(1C)	-9594(7)	-933(7)	255(13)	72(3)
C(2C)	-8267(5)	-679(5)	127(8)	44(2)
C(3C)	-7529(5)	-97(6)	-36(9)	53(2)
C(4C)	-6976(5)	-294(5)	-295(8)	45(2)
C(5C)	-7161(6)	-1043(6)	-369(8)	52(2)
C(6C)	-7891(5)	-1627(6)	-161(8)	50(2)
C(7C)	-8469(5)	-1453(5)	89(8)	45(2)
C(8C)	-9293(5)	-2042(5)	384(9)	49(2)
C(9C)	-9829(5)	-1744(6)	72(11)	62(3)
C(10C)	-10473(7)	-2274(9)	-452(15)	99(5)
C(11C)	-10526(7)	-3033(7)	-503(13)	75(3)
C(12C)	-9677(6)	-2836(5)	-248(9)	55(2)
C(13C)	-9637(7)	-3461(6)	352(9)	65(3)
C(14C)	-9353(12)	-4702(9)	618(13)	102(5)
C(15C)	-9856(11)	-5467(13)	243(18)	130(8)

Table 13. Bond lengths [Å] and angles [°] for crystal_04.

S(1)-C(13)	1.758(9)
S(1)-C(14)	1.830(12)
O(1)-C(1)	1.202(11)
O(2)-C(1)	1.358(10)
O(2)-C(2)	1.395(10)
O(3)-C(13)	1.194(11)
C(1)-C(9)	1.475(14)
C(2)-C(3)	1.384(12)
C(2)-C(7)	1.413(11)
C(3)-C(4)	1.378(13)
C(4)-C(5)	1.403(13)
C(5)-C(6)	1.410(12)
C(6)-C(7)	1.361(12)
C(7)-C(8)	1.489(11)
C(8)-C(9)	1.517(12)
C(8)-C(12)	1.550(11)
C(9)-C(10)	1.317(14)
C(10)-C(11)	1.473(16)
C(11)-C(12)	1.571(14)
C(12)-C(13)	1.506(13)
C(14)-C(15)	1.464(17)
S(1B)-C(13B)	1.726(14)
S(1B)-C(14B)	1.90(2)
S(1E)-C(13B)	1.698(16)
S(1E)-C(14E)	1.89(2)
O(1B)-C(1B)	1.211(13)
O(2B)-C(1B)	1.372(13)
O(2B)-C(2B)	1.405(11)
O(3B)-C(13B)	1.23(2)
O(3E)-C(13B)	1.238(19)
C(1B)-C(9B)	1.447(15)
C(2B)-C(3B)	1.400(14)
C(2B)-C(7B)	1.386(12)
C(3B)-C(4B)	1.394(16)
C(4B)-C(5B)	1.370(16)
C(5B)-C(6B)	1.384(15)
C(6B)-C(7B)	1.396(14)
C(7B)-C(8B)	1.515(12)
C(8B)-C(9B)	1.502(14)
C(8B)-C(12B)	1.510(13)
C(9B)-C(10B)	1.319(16)
C(10B)-C(11B)	1.488(18)
C(11B)-C(12B)	1.559(15)
C(12B)-C(13B)	1.557(14)
C(14B)-C(15B)	1.45(3)
C(14E)-C(15E)	1.44(3)

S(1A)-C(13A)	1.758(10)
S(1A)-C(14A)	1.842(17)
S(1D)-C(13A)	1.73(2)
S(1D)-C(14D)	1.84(3)
O(1A)-C(1A)	1.190(11)
O(2A)-C(1A)	1.370(10)
O(2A)-C(2A)	1.406(9)
O(3A)-C(13A)	1.174(12)
C(1A)-C(9A)	1.461(12)
C(2A)-C(3A)	1.393(11)
C(2A)-C(7A)	1.377(11)
C(3A)-C(4A)	1.385(13)
C(4A)-C(5A)	1.337(14)
C(5A)-C(6A)	1.403(13)
C(6A)-C(7A)	1.426(11)
C(7A)-C(8A)	1.498(11)
C(8A)-C(9A)	1.518(11)
C(8A)-C(12A)	1.544(11)
C(9A)-C(10A)	1.295(13)
C(10A)-C(11A)	1.563(14)
C(11A)-C(12A)	1.504(14)
C(12A)-C(13A)	1.520(11)
C(14A)-C(15A)	1.46(3)
C(14D)-C(15D)	1.47(4)
S(1C)-C(13C)	1.62(2)
S(1C)-C(14C)	1.98(4)
S(1F)-C(13C)	1.765(17)
S(1F)-C(14C)	1.848(15)
O(1C)-C(1C)	1.160(14)
O(2C)-C(1C)	1.385(13)
O(2C)-C(2C)	1.399(12)
O(3C)-C(13C)	1.231(13)
C(1C)-C(9C)	1.461(16)
C(2C)-C(3C)	1.360(13)
C(2C)-C(7C)	1.392(13)
C(3C)-C(4C)	1.381(14)
C(4C)-C(5C)	1.355(14)
C(5C)-C(6C)	1.362(14)
C(6C)-C(7C)	1.396(13)
C(7C)-C(8C)	1.511(12)
C(8C)-C(9C)	1.510(15)
C(8C)-C(12C)	1.564(13)
C(9C)-C(10C)	1.341(16)
C(10C)-C(11C)	1.47(2)
C(11C)-C(12C)	1.569(16)
C(12C)-C(13C)	1.473(16)
C(14C)-C(15C)	1.42(3)

C(13)-S(1)-C(14)	102.4(5)
C(1)-O(2)-C(2)	123.6(7)
O(1)-C(1)-O(2)	118.8(9)
O(1)-C(1)-C(9)	126.4(8)
O(2)-C(1)-C(9)	114.8(8)
O(2)-C(2)-C(7)	121.2(7)
C(3)-C(2)-O(2)	117.1(7)
C(3)-C(2)-C(7)	121.7(8)
C(4)-C(3)-C(2)	119.7(8)
C(3)-C(4)-C(5)	120.7(8)
C(4)-C(5)-C(6)	117.5(8)
C(7)-C(6)-C(5)	123.4(8)
C(2)-C(7)-C(8)	118.6(7)
C(6)-C(7)-C(2)	116.9(7)
C(6)-C(7)-C(8)	124.4(7)
C(7)-C(8)-C(9)	110.1(7)
C(7)-C(8)-C(12)	118.0(7)
C(9)-C(8)-C(12)	102.2(7)
C(1)-C(9)-C(8)	120.7(8)
C(10)-C(9)-C(1)	129.1(9)
C(10)-C(9)-C(8)	110.2(9)
C(9)-C(10)-C(11)	115.1(10)
C(10)-C(11)-C(12)	101.3(8)
C(8)-C(12)-C(11)	104.5(8)
C(13)-C(12)-C(8)	112.7(7)
C(13)-C(12)-C(11)	111.1(7)
O(3)-C(13)-S(1)	123.3(8)
O(3)-C(13)-C(12)	123.2(9)
C(12)-C(13)-S(1)	113.5(7)
C(15)-C(14)-S(1)	113.2(9)
C(13B)-S(1B)-C(14B)	100.3(14)
C(13B)-S(1E)-C(14E)	96.7(11)
C(1B)-O(2B)-C(2B)	120.9(7)
O(1B)-C(1B)-O(2B)	115.8(9)
O(1B)-C(1B)-C(9B)	127.0(10)
O(2B)-C(1B)-C(9B)	117.1(9)
C(3B)-C(2B)-O(2B)	113.3(8)
C(7B)-C(2B)-O(2B)	123.6(8)
C(7B)-C(2B)-C(3B)	123.1(9)
C(4B)-C(3B)-C(2B)	117.1(9)
C(5B)-C(4B)-C(3B)	120.5(11)
C(4B)-C(5B)-C(6B)	121.7(10)
C(5B)-C(6B)-C(7B)	119.6(9)
C(2B)-C(7B)-C(6B)	117.9(9)
C(2B)-C(7B)-C(8B)	117.3(8)
C(6B)-C(7B)-C(8B)	124.7(8)
C(9B)-C(8B)-C(7B)	111.6(7)
C(9B)-C(8B)-C(12B)	103.8(8)

C(12B)-C(8B)-C(7B)	116.9(8)
C(1B)-C(9B)-C(8B)	120.9(9)
C(10B)-C(9B)-C(1B)	126.7(11)
C(10B)-C(9B)-C(8B)	111.7(10)
C(9B)-C(10B)-C(11B)	111.4(10)
C(10B)-C(11B)-C(12B)	102.8(8)
C(8B)-C(12B)-C(11B)	104.0(9)
C(8B)-C(12B)-C(13B)	113.7(8)
C(13B)-C(12B)-C(11B)	111.8(9)
O(3B)-C(13B)-S(1B)	119.5(15)
O(3B)-C(13B)-C(12B)	127.3(15)
O(3E)-C(13B)-S(1E)	123.6(14)
O(3E)-C(13B)-C(12B)	118.7(15)
C(12B)-C(13B)-S(1B)	112.4(8)
C(12B)-C(13B)-S(1E)	116.4(9)
C(15B)-C(14B)-S(1B)	92.5(19)
C(15E)-C(14E)-S(1E)	109.9(19)
C(13A)-S(1A)-C(14A)	102.0(8)
C(13A)-S(1D)-C(14D)	88(4)
C(1A)-O(2A)-C(2A)	120.4(6)
O(1A)-C(1A)-O(2A)	117.3(8)
O(1A)-C(1A)-C(9A)	126.0(8)
O(2A)-C(1A)-C(9A)	116.6(7)
C(3A)-C(2A)-O(2A)	114.3(7)
C(7A)-C(2A)-O(2A)	122.5(7)
C(7A)-C(2A)-C(3A)	123.2(7)
C(4A)-C(3A)-C(2A)	117.1(8)
C(5A)-C(4A)-C(3A)	122.4(8)
C(4A)-C(5A)-C(6A)	120.9(9)
C(5A)-C(6A)-C(7A)	118.8(8)
C(2A)-C(7A)-C(6A)	117.5(7)
C(2A)-C(7A)-C(8A)	119.8(7)
C(6A)-C(7A)-C(8A)	122.6(7)
C(7A)-C(8A)-C(9A)	109.5(6)
C(7A)-C(8A)-C(12A)	119.3(7)
C(9A)-C(8A)-C(12A)	102.0(7)
C(1A)-C(9A)-C(8A)	121.0(7)
C(10A)-C(9A)-C(1A)	126.7(8)
C(10A)-C(9A)-C(8A)	112.2(8)
C(9A)-C(10A)-C(11A)	109.8(9)
C(12A)-C(11A)-C(10A)	102.1(7)
C(11A)-C(12A)-C(8A)	103.8(7)
C(11A)-C(12A)-C(13A)	110.5(8)
C(13A)-C(12A)-C(8A)	111.7(7)
O(3A)-C(13A)-S(1A)	121.1(7)
O(3A)-C(13A)-S(1D)	117.2(12)
O(3A)-C(13A)-C(12A)	126.0(9)
C(12A)-C(13A)-S(1A)	112.9(7)

C(12A)-C(13A)-S(1D)	110.7(11)
C(15A)-C(14A)-S(1A)	112.6(14)
C(15D)-C(14D)-S(1D)	109(6)
C(13C)-S(1C)-C(14C)	103(2)
C(13C)-S(1F)-C(14C)	103.0(9)
C(1C)-O(2C)-C(2C)	122.9(8)
O(1C)-C(1C)-O(2C)	117.4(11)
O(1C)-C(1C)-C(9C)	128.1(11)
O(2C)-C(1C)-C(9C)	114.3(9)
C(3C)-C(2C)-O(2C)	115.9(8)
C(3C)-C(2C)-C(7C)	122.3(9)
C(7C)-C(2C)-O(2C)	121.7(8)
C(2C)-C(3C)-C(4C)	118.0(9)
C(5C)-C(4C)-C(3C)	120.9(8)
C(4C)-C(5C)-C(6C)	121.4(9)
C(5C)-C(6C)-C(7C)	119.4(9)
C(2C)-C(7C)-C(6C)	117.9(8)
C(2C)-C(7C)-C(8C)	117.2(8)
C(6C)-C(7C)-C(8C)	124.8(8)
C(7C)-C(8C)-C(12C)	118.3(8)
C(9C)-C(8C)-C(7C)	110.5(8)
C(9C)-C(8C)-C(12C)	101.5(8)
C(1C)-C(9C)-C(8C)	120.3(9)
C(10C)-C(9C)-C(1C)	126.5(12)
C(10C)-C(9C)-C(8C)	113.0(11)
C(9C)-C(10C)-C(11C)	112.4(12)
C(10C)-C(11C)-C(12C)	102.8(9)
C(8C)-C(12C)-C(11C)	105.5(9)
C(13C)-C(12C)-C(8C)	115.3(9)
C(13C)-C(12C)-C(11C)	113.0(9)
O(3C)-C(13C)-S(1C)	118.5(11)
O(3C)-C(13C)-S(1F)	122.2(11)
O(3C)-C(13C)-C(12C)	120.3(12)
C(12C)-C(13C)-S(1C)	115.8(14)
C(12C)-C(13C)-S(1F)	117.4(8)
C(15C)-C(14C)-S(1C)	100.3(18)
C(15C)-C(14C)-S(1F)	115.6(13)

Table 14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal_04. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

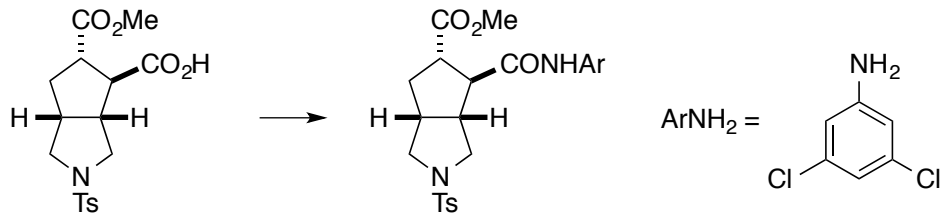
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	60(2)	60(2)	51(1)	-5(1)	-10(1)	16(1)
O(1)	37(4)	54(4)	109(6)	18(4)	1(4)	25(3)
O(2)	40(3)	35(3)	61(4)	0(3)	-1(3)	16(3)
O(3)	75(5)	58(4)	39(4)	10(3)	-4(3)	-1(4)
C(1)	42(5)	48(5)	61(6)	6(4)	0(4)	28(4)
C(2)	33(4)	28(4)	51(5)	-5(3)	-6(3)	15(3)
C(3)	39(5)	32(4)	59(6)	-4(4)	1(4)	15(4)
C(4)	48(5)	44(5)	69(6)	19(4)	9(4)	31(4)
C(5)	35(4)	44(5)	64(6)	-6(4)	-1(4)	21(4)
C(6)	33(4)	28(4)	63(5)	-1(4)	3(4)	14(3)
C(7)	40(4)	25(4)	41(4)	1(3)	-4(3)	13(3)
C(8)	37(4)	34(4)	39(4)	2(3)	5(3)	18(3)
C(9)	42(5)	40(5)	71(6)	10(4)	12(4)	23(4)
C(10)	66(7)	44(5)	107(10)	16(6)	24(6)	38(5)
C(11)	72(7)	49(6)	81(8)	3(5)	15(6)	40(5)
C(12)	61(6)	28(4)	50(5)	4(4)	12(4)	23(4)
C(13)	48(5)	35(4)	45(5)	-2(4)	-6(4)	18(4)
C(14)	52(6)	63(7)	75(7)	-18(6)	0(5)	16(5)
C(15)	50(6)	71(7)	61(6)	-7(5)	-19(5)	23(5)
S(1B)	53(5)	39(4)	57(4)	-9(3)	6(3)	11(3)
S(1E)	71(6)	74(6)	76(5)	17(4)	-3(4)	12(4)
O(1B)	34(4)	58(5)	163(10)	9(5)	-4(5)	18(4)
O(2B)	33(3)	31(3)	78(5)	5(3)	4(3)	7(2)
O(3B)	84(16)	66(13)	63(11)	-26(9)	26(10)	-5(11)
O(3E)	85(16)	71(13)	74(9)	22(9)	4(9)	-7(10)
C(1B)	54(6)	37(5)	98(9)	22(5)	11(6)	18(5)
C(2B)	47(5)	40(5)	46(5)	6(4)	11(4)	18(4)
C(3B)	49(5)	38(5)	54(6)	11(4)	6(4)	8(4)
C(4B)	71(7)	61(6)	56(6)	0(5)	4(5)	35(6)
C(5B)	49(6)	66(7)	71(7)	-2(5)	-2(5)	30(5)
C(6B)	59(6)	46(5)	47(5)	-2(4)	7(4)	20(5)
C(7B)	45(5)	37(4)	43(5)	-1(4)	-3(4)	14(4)
C(8B)	43(5)	29(4)	64(6)	16(4)	7(4)	11(4)
C(9B)	51(6)	48(5)	79(7)	10(5)	3(5)	24(5)
C(10B)	67(7)	66(7)	107(10)	16(7)	38(7)	37(6)
C(11B)	80(8)	45(6)	128(12)	7(7)	41(8)	35(6)
C(12B)	47(5)	29(4)	64(6)	0(4)	4(4)	10(4)
C(13B)	70(6)	44(5)	52(5)	-9(4)	12(5)	11(4)
C(14B)	48(10)	66(10)	80(13)	15(10)	11(9)	23(8)
C(14E)	77(13)	65(11)	65(11)	9(8)	11(11)	0(10)
C(15B)	77(17)	66(15)	120(20)	23(14)	26(15)	28(13)
C(15E)	51(13)	55(10)	117(17)	14(11)	-1(12)	5(9)
S(1A)	59(3)	133(6)	45(2)	-7(2)	-12(2)	64(4)

S(1D) 88(11)	102(13)	94(11)	10(11)	-7(9)	71(10)
O(1A) 33(3)	53(4)	92(6)	-11(4)	-11(3)	16(3)
O(2A) 35(3)	39(3)	53(3)	-2(3)	-6(3)	20(3)
O(3A) 88(6)	228(13)	44(4)	15(6)	20(4)	117(8)
C(1A) 36(4)	41(4)	48(5)	-5(4)	2(4)	19(4)
C(2A) 29(4)	39(4)	25(3)	8(3)	3(3)	15(3)
C(3A) 50(5)	42(5)	51(5)	14(4)	16(4)	35(4)
C(4A) 58(6)	27(4)	56(6)	5(4)	-3(4)	17(4)
C(5A) 41(5)	42(5)	53(5)	4(4)	6(4)	12(4)
C(6A) 32(4)	60(5)	34(4)	5(4)	5(3)	24(4)
C(7A) 32(4)	37(4)	24(3)	8(3)	6(3)	19(3)
C(8A) 31(4)	45(4)	33(4)	-2(3)	3(3)	22(3)
C(9A) 34(4)	39(4)	43(4)	-7(3)	-3(3)	18(4)
C(10A)46(5)	40(5)	82(7)	3(5)	13(5)	21(4)
C(11A)76(7)	69(7)	52(6)	8(5)	12(5)	54(6)
C(12A)45(5)	49(5)	40(4)	6(4)	8(4)	30(4)
C(13A)44(5)	60(6)	51(5)	10(4)	9(4)	40(5)
C(14A)62(8)	119(10)	83(9)	-4(8)	-7(7)	63(8)
C(14D)81(16)	117(15)	88(15)	-5(14)	-5(13)	76(14)
C(15A)111(12)	128(13)	112(14)	22(11)	49(11)	94(11)
C(15D)100(20)	130(20)	100(20)	-20(20)	-6(19)	70(20)
S(1C) 70(20)	70(10)	92(11)	0(9)	42(11)	32(12)
S(1F) 86(9)	66(4)	65(3)	11(2)	18(3)	46(5)
O(1C) 45(4)	72(6)	216(14)	-13(7)	-19(6)	35(4)
O(2C) 38(3)	40(3)	93(5)	-1(3)	-4(3)	19(3)
O(3C)175(11)	84(6)	73(6)	31(5)	52(7)	67(7)
C(1C) 49(6)	63(7)	103(10)	-4(6)	-9(6)	27(6)
C(2C) 44(5)	34(4)	47(5)	0(4)	-11(4)	13(4)
C(3C) 39(5)	41(5)	65(6)	2(4)	8(4)	11(4)
C(4C) 28(4)	45(5)	46(5)	0(4)	5(3)	6(4)
C(5C) 46(5)	69(6)	50(5)	8(5)	9(4)	35(5)
C(6C) 45(5)	47(5)	52(5)	2(4)	13(4)	19(4)
C(7C) 40(5)	41(5)	55(5)	1(4)	0(4)	21(4)
C(8C) 42(5)	39(5)	59(6)	3(4)	5(4)	15(4)
C(9C) 34(5)	39(5)	96(8)	-6(5)	-11(5)	5(4)
C(10C)46(6)	84(9)	137(13)	23(9)	-32(7)	10(6)
C(11C)58(7)	47(6)	98(10)	-6(6)	-11(6)	9(5)
C(12C)49(5)	35(5)	59(6)	-3(4)	6(4)	4(4)
C(13C)70(7)	37(5)	44(5)	1(4)	10(5)	-7(5)
C(14C)171(17)	82(10)	79(9)	9(8)	-14(10)	83(12)
C(15C)113(14)	153(19)	138(16)	81(15)	38(12)	76(14)

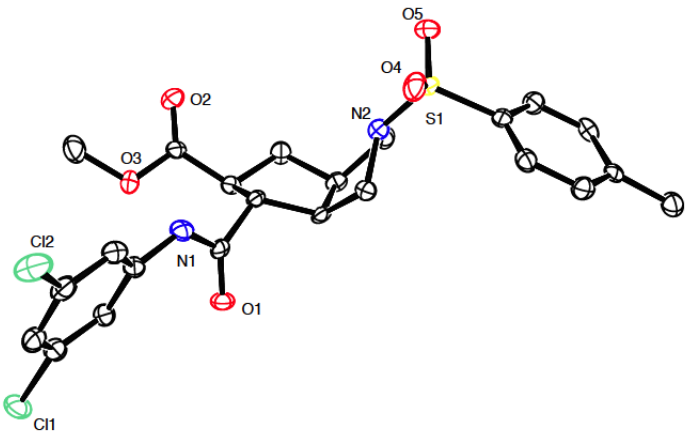
Table 15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal_04.

	x	y	z	U(eq)
H(3)	-9494	-8779	-3553	54
H(4)	-8250	-8499	-3097	60
H(5)	-7253	-7203	-2881	56
H(6)	-7538	-6215	-3234	50
H(8)	-8756	-6129	-4643	43
H(10)	-10312	-6097	-3014	81
H(11G)	-9096	-5067	-2231	76
H(11H)	-9035	-4897	-3580	76
H(12)	-8348	-5642	-2328	55
H(14M)	-5685	-3651	-3314	83
H(14N)	-6250	-3967	-4387	83
H(15P)	-6581	-3070	-4221	95
H(15Q)	-5679	-2611	-3936	95
H(15R)	-6298	-2887	-2929	95
H(3B)	-9456	-13754	-3228	64
H(4B)	-8164	-13444	-2941	73
H(5B)	-7186	-12175	-2956	74
H(6B)	-7430	-11178	-3344	64
H(8B)	-8753	-11146	-4589	58
H(10B)	-10260	-11098	-2766	94
H(11A)	-8987	-10015	-2214	99
H(11B)	-9011	-9912	-3570	99
H(12B)	-8259	-10600	-2357	61
H(14A)	-5742	-8433	-3424	80
H(14B)	-6271	-8833	-4543	80
H(14C)	-6137	-8593	-4535	101
H(14D)	-6829	-8413	-4408	101
H(15A)	-5971	-7543	-4480	135
H(15B)	-6289	-7664	-3205	135
H(15C)	-6872	-8092	-4234	135
H(15D)	-6224	-7630	-2882	126
H(15E)	-5659	-7347	-3958	126
H(15F)	-5543	-7827	-2966	126
H(3A)	-2158	-7616	-2977	51
H(4A)	-3439	-8583	-3266	58
H(5A)	-4404	-8307	-3392	59
H(6A)	-4167	-7044	-3085	50
H(8A)	-2871	-5684	-1775	42
H(10A)	-1326	-4138	-3522	68
H(11C)	-2643	-4256	-2686	69
H(11D)	-2628	-4294	-4055	69
H(12A)	-3294	-5601	-4087	50

H(14E)	-5920	-6042	-3166	96
H(14F)	-5426	-6004	-2074	96
H(14G)	-5736	-5948	-3166	100
H(14H)	-5247	-6186	-2350	100
H(15G)	-5170	-4656	-3190	152
H(15H)	-4889	-4722	-1943	152
H(15I)	-5784	-5032	-2182	152
H(15J)	-4779	-4733	-1858	153
H(15K)	-5306	-5463	-1071	153
H(15L)	-5699	-5146	-1939	153
H(3C)	-7399	428	26	63
H(4C)	-6458	102	-422	54
H(5C)	-6773	-1163	-570	63
H(6C)	-8007	-2148	-186	60
H(8C)	-9328	-2138	1221	59
H(10C)	-10852	-2171	-755	119
H(11E)	-10695	-3269	-1264	90
H(11F)	-10889	-3387	76	90
H(12C)	-9408	-2756	-993	66
H(14I)	-8804	-4557	533	122
H(14J)	-9454	-4627	1418	122
H(14K)	-8842	-4647	776	122
H(14L)	-9554	-4623	1344	122
H(15M)	-10389	-5569	251	196
H(15N)	-9811	-5831	750	196
H(15O)	-9716	-5529	-532	196



Methyl (3a*R*,4*S*,5*S*,6a*R*)-4-((3,5-dichlorophenyl)carbamoyl)-2-tosyloctahydrocyclopenta[*c*]pyrrole-5-carboxylate (derived from the product of eq 6). (3a*R*,4*S*,5*S*,6a*R*)-5-(Methoxycarbonyl)-2-tosyloctahydrocyclopenta[*c*]pyrrole-4-carboxylic acid (7.35 mg, 0.020 mmol), 4-dimethylaminopyridine (1.0 mg, 0.0080 mmol), 3,5-dichloroaniline (4.0 mg, 0.025 mmol), and CH_2Cl_2 (0.20 mL) were added to a 4-mL vial equipped with a stir bar. The mixture was cooled to 0 °C, and a solution of *N*,*N*′-dicyclohexylcarbodiimide (5.0 mg, 0.024 mmol) in CH_2Cl_2 (0.10 mL) was added dropwise. The reaction mixture was stirred at r.t. for 12 h. Then, the mixture was filtered through a short pad of celite and concentrated under reduced pressure. The residue was purified by preparative TLC, which afforded the title compound as a white crystalline solid. X-ray quality crystals were grown from CH_2Cl_2/pentane.



A suitable crystal of $C_{23}H_{24}Cl_2N_2O_5S$ was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[1] the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[2] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J Appl Crystallogr* **2009**, *42*, 339.
2. Sheldrick, G. M. *Acta Crystallogr A* **2008**, *64*, 112.

Table 16. Crystal data and structure refinement for crystal_06.

Identification code	crystal_06	
Empirical formula	$C_{23}H_{24}Cl_2N_2O_5S$	
Formula weight	510.41	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 11.4993(3) Å	$\alpha = 90°$
	b = 38.6548(10) Å	$\beta = 90°$
	c = 5.15110(10) Å	$\gamma = 90°$
Volume	2289.68(10) $Å^3$	
Z	4	
Density (calculated)	1.481 Mg/m^3	
Absorption coefficient	3.724 mm^{-1}	
F(000)	1064	
Crystal size	0.14 x 0.04 x 0.02 mm^3	
Theta range for data collection	4.011 to 70.062°.	
Index ranges	-14<=h<=13, -47<=k<=47, -6<=l<=6	
Reflections collected	49329	
Independent reflections	4363 [R(int) = 0.1475]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7208 and 0.6318	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4363 / 0 / 300	
Goodness-of-fit on F^2	1.168	
Final R indices [I>2sigma(I)]	R1 = 0.0601, wR2 = 0.1464	
R indices (all data)	R1 = 0.0690, wR2 = 0.1505	
Absolute structure parameter	0.081(12)	
Largest diff. peak and hole	0.702 and -0.351 $e/Å^{-3}$	

Table 17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal_06. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	-7084(2)	-2821(1)	5281(4)	33(1)
Cl(2)	-9871(2)	-3198(1)	-2607(3)	34(1)
S(1)	-13276(1)	-793(1)	-1993(3)	24(1)
O(1)	-9547(4)	-1741(1)	4572(9)	22(1)
O(2)	-7863(4)	-1031(1)	-2808(10)	26(1)
O(3)	-7478(4)	-1496(1)	-348(10)	26(1)
O(4)	-13664(4)	-1125(1)	-2926(10)	29(1)
O(5)	-13000(5)	-524(1)	-3790(9)	33(1)
N(1)	-9673(5)	-1948(1)	446(11)	19(1)
N(2)	-12087(5)	-865(1)	-327(11)	22(1)
C(1)	-8856(6)	-1102(2)	1266(13)	18(1)
C(2)	-9370(6)	-740(2)	954(14)	23(2)
C(3)	-10515(6)	-742(2)	2474(13)	21(1)
C(4)	-11538(6)	-569(2)	997(14)	24(2)
C(5)	-12091(6)	-1155(2)	1543(13)	20(1)
C(6)	-10875(5)	-1129(2)	2722(13)	18(1)
C(7)	-9964(5)	-1335(2)	1178(12)	15(1)
C(8)	-8018(6)	-1195(2)	-852(13)	18(1)
C(9)	-9719(5)	-1690(2)	2264(12)	16(1)
C(10)	-9295(6)	-2291(2)	837(14)	19(1)
C(11)	-9725(6)	-2546(2)	-786(13)	21(1)
C(12)	-9359(6)	-2884(2)	-491(14)	24(2)
C(13)	-8588(7)	-2978(2)	1411(14)	26(2)
C(14)	-8137(6)	-2719(2)	2962(14)	24(2)
C(15)	-8479(6)	-2375(2)	2733(13)	20(1)
C(16)	-6748(7)	-1627(2)	-2443(16)	33(2)
C(17)	-14344(5)	-629(2)	145(12)	20(1)
C(18)	-14434(6)	-279(2)	588(14)	23(1)
C(19)	-15248(6)	-157(2)	2340(14)	22(1)
C(20)	-15968(6)	-382(2)	3678(12)	18(1)
C(21)	-15870(6)	-734(2)	3163(13)	22(1)
C(22)	-15069(6)	-860(2)	1390(12)	21(1)
C(23)	-16815(6)	-254(2)	5670(14)	27(2)

Table 18. Bond lengths [Å] and angles [°] for crystal_06.

Cl(1)-C(14)	1.746(7)
Cl(2)-C(12)	1.734(7)
S(1)-O(4)	1.444(5)
S(1)-O(5)	1.426(5)
S(1)-N(2)	1.638(6)
S(1)-C(17)	1.767(7)
O(1)-C(9)	1.221(8)
O(2)-C(8)	1.202(8)
O(3)-C(8)	1.346(8)
O(3)-C(16)	1.458(9)
N(1)-C(9)	1.368(8)
N(1)-C(10)	1.412(8)
N(2)-C(4)	1.473(9)
N(2)-C(5)	1.479(8)
C(1)-C(2)	1.527(9)
C(1)-C(7)	1.561(9)
C(1)-C(8)	1.499(9)
C(2)-C(3)	1.532(9)
C(3)-C(4)	1.552(9)
C(3)-C(6)	1.559(9)
C(5)-C(6)	1.528(9)
C(6)-C(7)	1.537(8)
C(7)-C(9)	1.508(9)
C(10)-C(11)	1.382(9)
C(10)-C(15)	1.392(9)
C(11)-C(12)	1.381(10)
C(12)-C(13)	1.371(11)
C(13)-C(14)	1.380(11)
C(14)-C(15)	1.393(9)
C(17)-C(18)	1.376(10)
C(17)-C(22)	1.381(9)
C(18)-C(19)	1.382(10)
C(19)-C(20)	1.383(9)
C(20)-C(21)	1.391(10)
C(20)-C(23)	1.499(9)
C(21)-C(22)	1.386(9)

O(4)-S(1)-N(2)	106.3(3)
O(4)-S(1)-C(17)	108.2(3)
O(5)-S(1)-O(4)	120.0(3)
O(5)-S(1)-N(2)	106.1(3)
O(5)-S(1)-C(17)	107.4(3)
N(2)-S(1)-C(17)	108.3(3)
C(8)-O(3)-C(16)	115.0(5)
C(9)-N(1)-C(10)	126.8(6)
C(4)-N(2)-S(1)	117.9(4)

C(4)-N(2)-C(5)	106.8(5)
C(5)-N(2)-S(1)	117.9(5)
C(2)-C(1)-C(7)	102.1(5)
C(8)-C(1)-C(2)	113.0(5)
C(8)-C(1)-C(7)	111.4(5)
C(1)-C(2)-C(3)	106.0(5)
C(2)-C(3)-C(4)	113.5(5)
C(2)-C(3)-C(6)	105.9(5)
C(4)-C(3)-C(6)	104.6(5)
N(2)-C(4)-C(3)	102.6(5)
N(2)-C(5)-C(6)	101.9(5)
C(5)-C(6)-C(3)	105.9(5)
C(5)-C(6)-C(7)	112.6(5)
C(7)-C(6)-C(3)	105.9(5)
C(6)-C(7)-C(1)	104.0(5)
C(9)-C(7)-C(1)	111.2(5)
C(9)-C(7)-C(6)	114.0(5)
O(2)-C(8)-O(3)	123.2(6)
O(2)-C(8)-C(1)	125.4(6)
O(3)-C(8)-C(1)	111.3(5)
O(1)-C(9)-N(1)	122.8(6)
O(1)-C(9)-C(7)	122.6(6)
N(1)-C(9)-C(7)	114.5(5)
C(11)-C(10)-N(1)	118.2(6)
C(11)-C(10)-C(15)	120.1(6)
C(15)-C(10)-N(1)	121.7(6)
C(12)-C(11)-C(10)	119.8(7)
C(11)-C(12)-Cl(2)	119.3(6)
C(13)-C(12)-Cl(2)	118.9(6)
C(13)-C(12)-C(11)	121.7(7)
C(12)-C(13)-C(14)	117.8(7)
C(13)-C(14)-Cl(1)	119.5(5)
C(13)-C(14)-C(15)	122.4(7)
C(15)-C(14)-Cl(1)	118.0(6)
C(10)-C(15)-C(14)	118.1(6)
C(18)-C(17)-S(1)	120.6(5)
C(18)-C(17)-C(22)	120.9(6)
C(22)-C(17)-S(1)	118.5(5)
C(17)-C(18)-C(19)	119.6(6)
C(18)-C(19)-C(20)	121.2(6)
C(19)-C(20)-C(21)	118.0(6)
C(19)-C(20)-C(23)	121.5(6)
C(21)-C(20)-C(23)	120.4(6)
C(22)-C(21)-C(20)	121.6(6)
C(17)-C(22)-C(21)	118.7(6)

Table 19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal_06. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

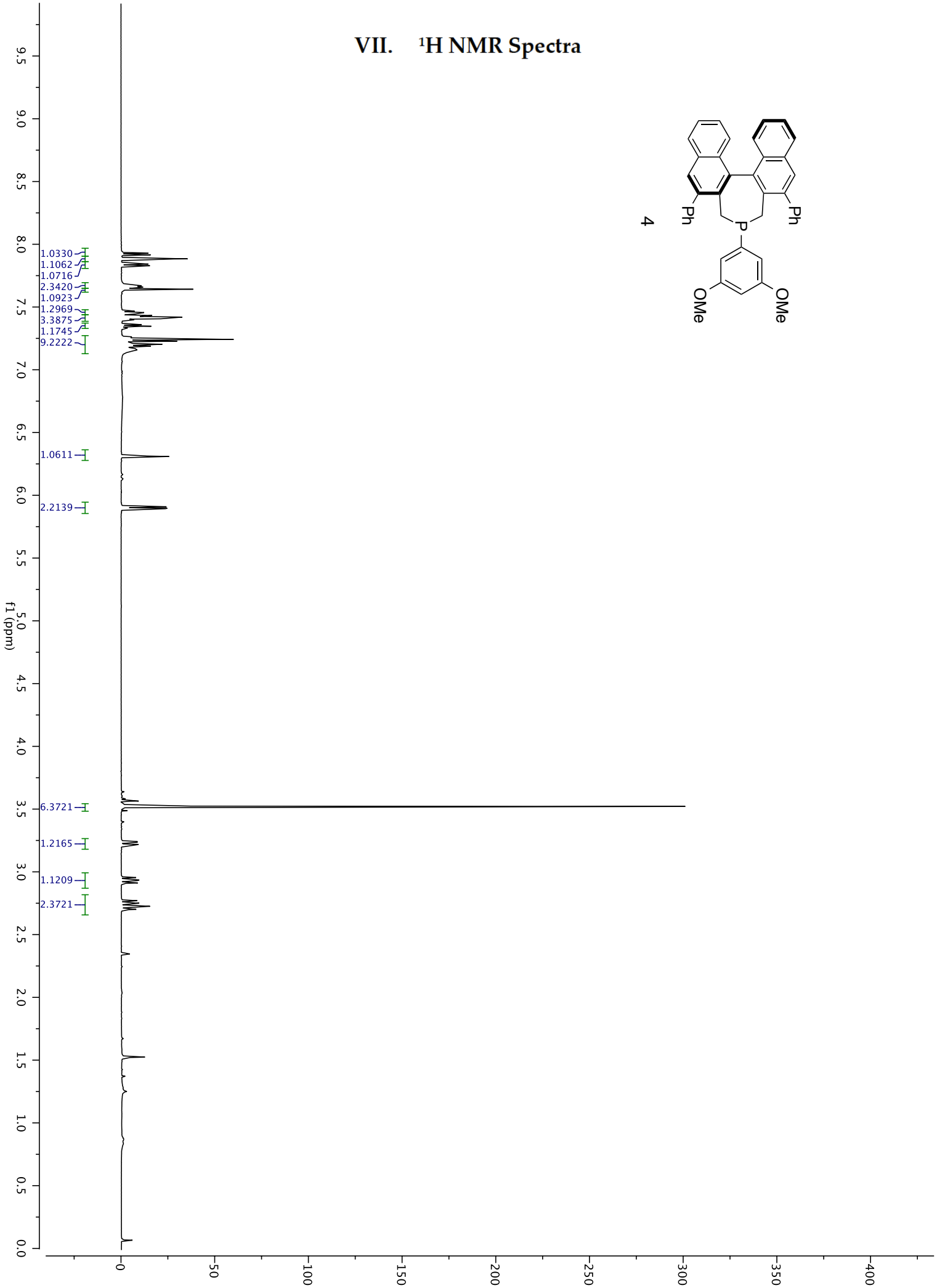
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	22(1)	43(1)	34(1)	16(1)	-2(1)	7(1)
Cl(2)	57(1)	21(1)	22(1)	-3(1)	6(1)	-10(1)
S(1)	21(1)	36(1)	14(1)	2(1)	2(1)	7(1)
O(1)	23(2)	28(3)	15(2)	5(2)	-2(2)	0(2)
O(2)	25(3)	32(3)	23(2)	4(2)	6(2)	-1(2)
O(3)	22(2)	29(3)	27(3)	2(2)	6(2)	7(2)
O(4)	26(3)	39(3)	23(3)	-11(2)	0(2)	7(2)
O(5)	28(3)	48(3)	22(3)	14(2)	3(2)	7(3)
N(1)	18(3)	24(3)	16(3)	1(2)	-5(2)	-1(2)
N(2)	20(3)	27(3)	19(3)	2(2)	2(2)	2(2)
C(1)	18(3)	19(3)	18(3)	2(3)	-1(3)	-1(3)
C(2)	22(4)	18(3)	30(4)	2(3)	4(3)	-2(3)
C(3)	24(3)	22(3)	17(3)	-2(3)	1(3)	-2(3)
C(4)	21(4)	22(3)	27(4)	3(3)	8(3)	3(3)
C(5)	19(3)	22(3)	19(3)	2(3)	0(3)	1(3)
C(6)	20(3)	19(3)	15(3)	3(3)	7(3)	-1(2)
C(7)	13(3)	21(3)	12(3)	1(2)	1(2)	-1(3)
C(8)	13(3)	25(3)	17(3)	4(3)	-2(3)	-2(3)
C(9)	10(3)	22(3)	17(3)	1(3)	2(3)	-3(2)
C(10)	19(3)	17(3)	20(3)	3(3)	3(3)	0(3)
C(11)	22(4)	23(3)	19(3)	2(3)	0(3)	-2(3)
C(12)	27(4)	23(4)	20(3)	-1(3)	8(3)	-2(3)
C(13)	28(4)	24(4)	27(4)	5(3)	11(3)	4(3)
C(14)	20(3)	26(4)	26(3)	7(3)	6(3)	2(3)
C(15)	17(3)	24(3)	20(3)	2(3)	0(3)	2(3)
C(16)	27(4)	39(4)	33(4)	-4(4)	-6(3)	10(3)
C(17)	16(3)	33(4)	11(3)	-1(3)	-4(2)	2(3)
C(18)	20(3)	24(3)	25(4)	3(3)	1(3)	-1(3)
C(19)	19(3)	19(3)	27(4)	-1(3)	-7(3)	3(3)
C(20)	15(3)	24(3)	14(3)	0(3)	-6(2)	3(3)
C(21)	18(3)	25(4)	23(3)	3(3)	0(3)	-4(3)
C(22)	21(3)	20(3)	22(3)	-1(3)	-2(3)	4(3)
C(23)	26(4)	29(4)	25(4)	-2(3)	-1(3)	7(3)

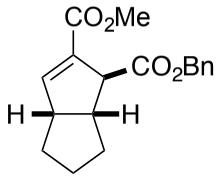
Table 20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal_06.

	x	y	z	U(eq)
H(1)	-9903	-1894	-1132	23
H(1A)	-8468	-1123	2997	22
H(2A)	-9514	-689	-901	28
H(2B)	-8833	-564	1662	28
H(3)	-10410	-635	4226	25
H(4A)	-12086	-456	2212	28
H(4B)	-11253	-396	-268	28
H(5A)	-12207	-1380	655	24
H(5B)	-12702	-1125	2878	24
H(6)	-10883	-1203	4583	22
H(7)	-10230	-1358	-662	18
H(11)	-10272	-2488	-2100	26
H(13)	-8371	-3212	1654	32
H(15)	-8164	-2202	3839	24
H(16A)	-7170	-1611	-4090	49
H(16B)	-6548	-1869	-2101	49
H(16C)	-6034	-1489	-2545	49
H(18)	-13940	-122	-304	28
H(19)	-15313	85	2630	26
H(21)	-16365	-892	4048	27
H(22)	-15020	-1101	1039	25
H(23A)	-16467	-271	7401	40
H(23B)	-17524	-394	5603	40
H(23C)	-17009	-11	5308	40

VII. ^{1}H NMR Spectra

4





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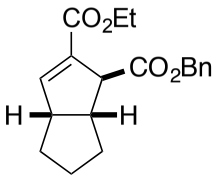


Table 1, entry 2

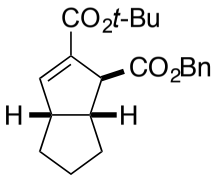
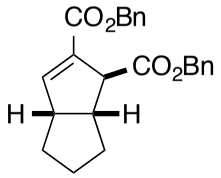


Table 1, entry 3



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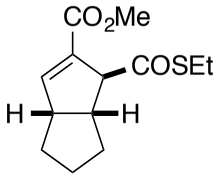

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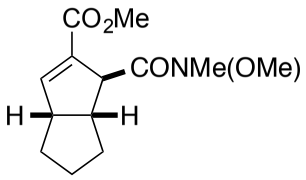

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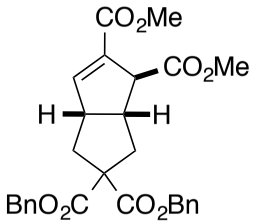
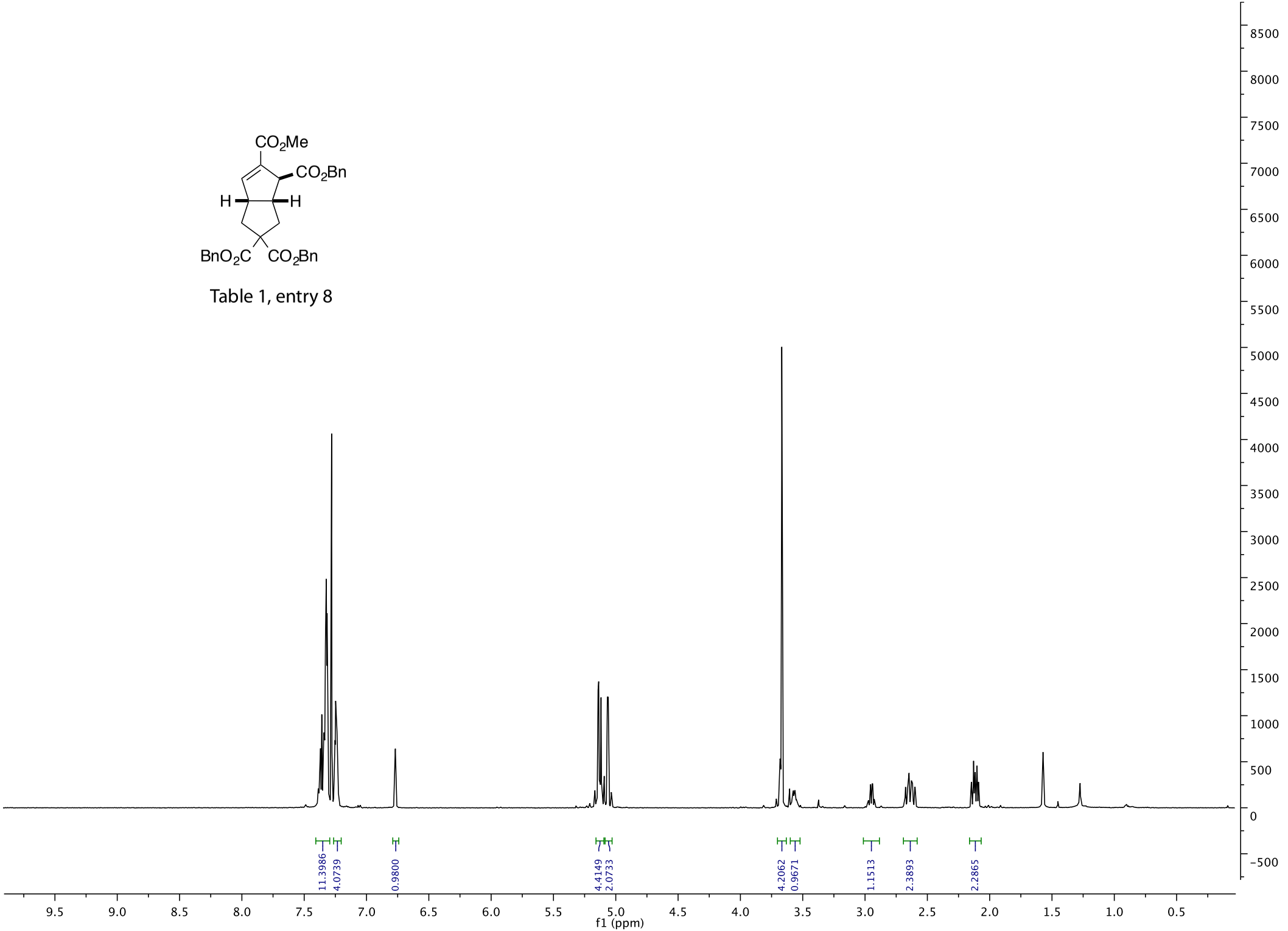
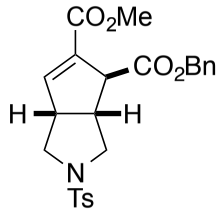


Table 1, entry 7

Table 1, entry 8





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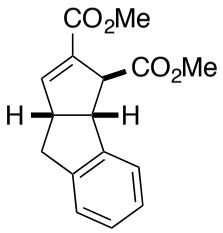
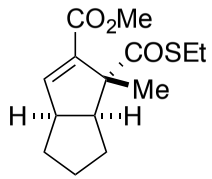


Table 1, entry 10



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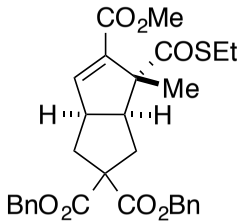
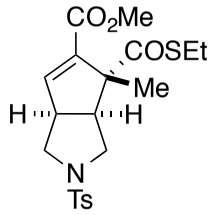


Table 2, entry 2



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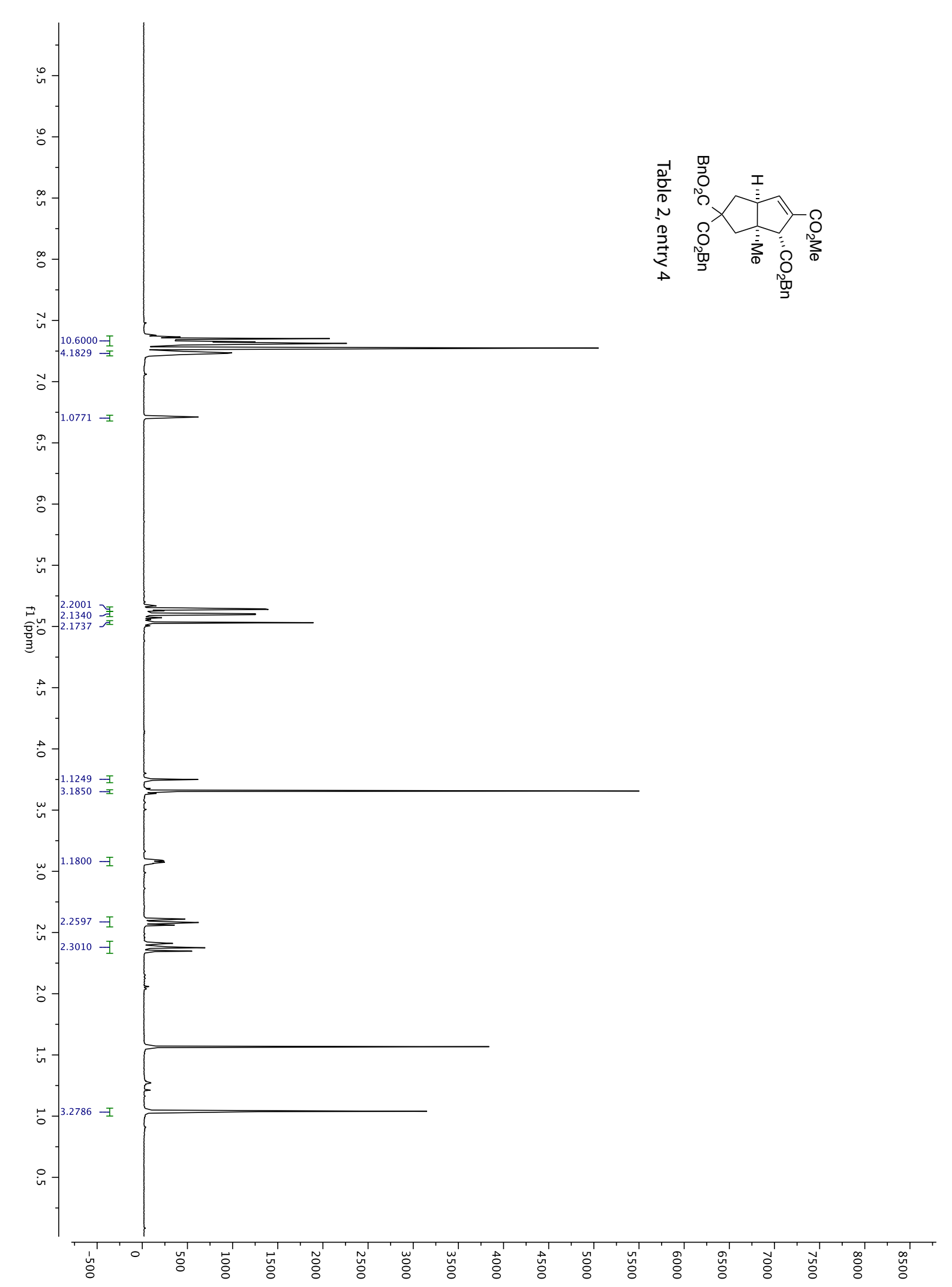
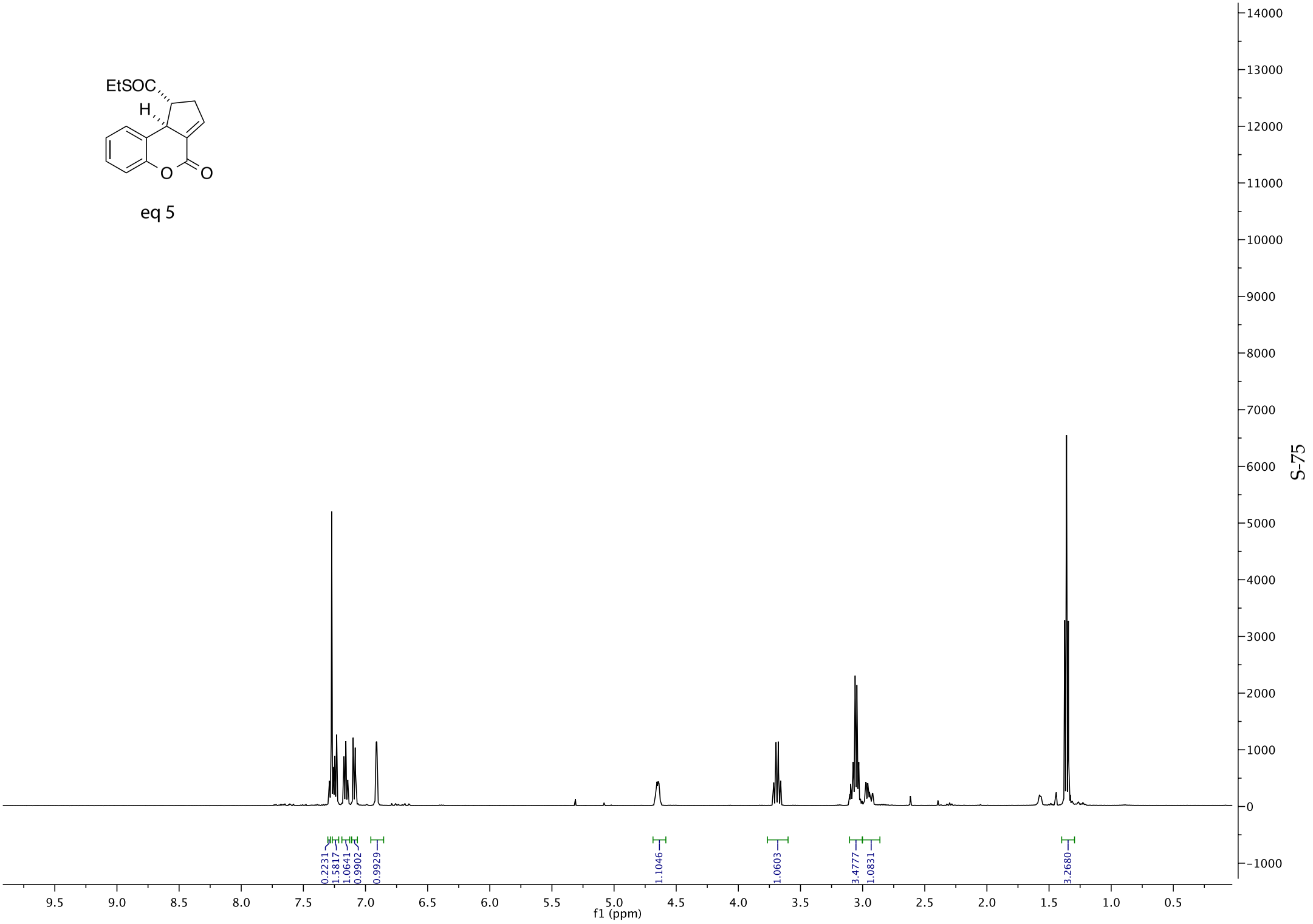
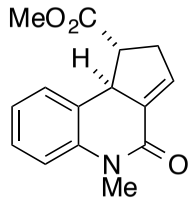


Table 2, entry 4
BnO2C
CO2Bn
H
Me
CO2Bn
CO2Me
f1 (ppm)
10.6000
4.1829
1.0771
2.2001
2.1340
2.1737
1.1249
3.1850
1.1800
2.2597
2.3010
3.2786

EtSOC
H
O
O

eq 5


0.2231
1.5817
1.0641
0.9902
0.9929
1.1046
1.0603
3.4777
1.0831
3.2680
f1 (ppm)



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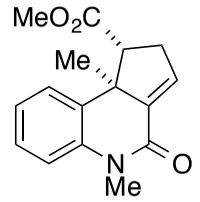
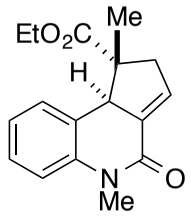


Table 3, entry 2



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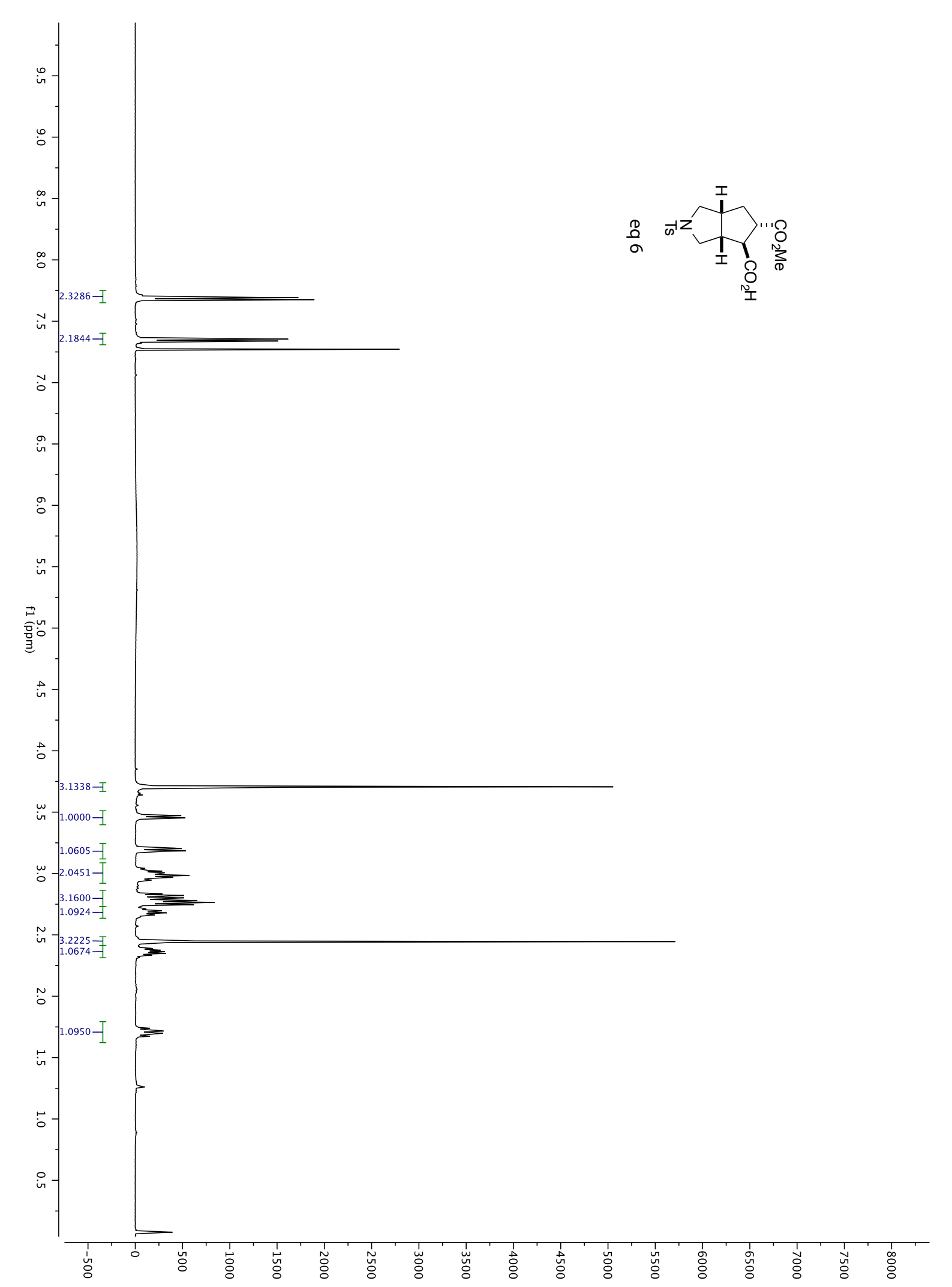
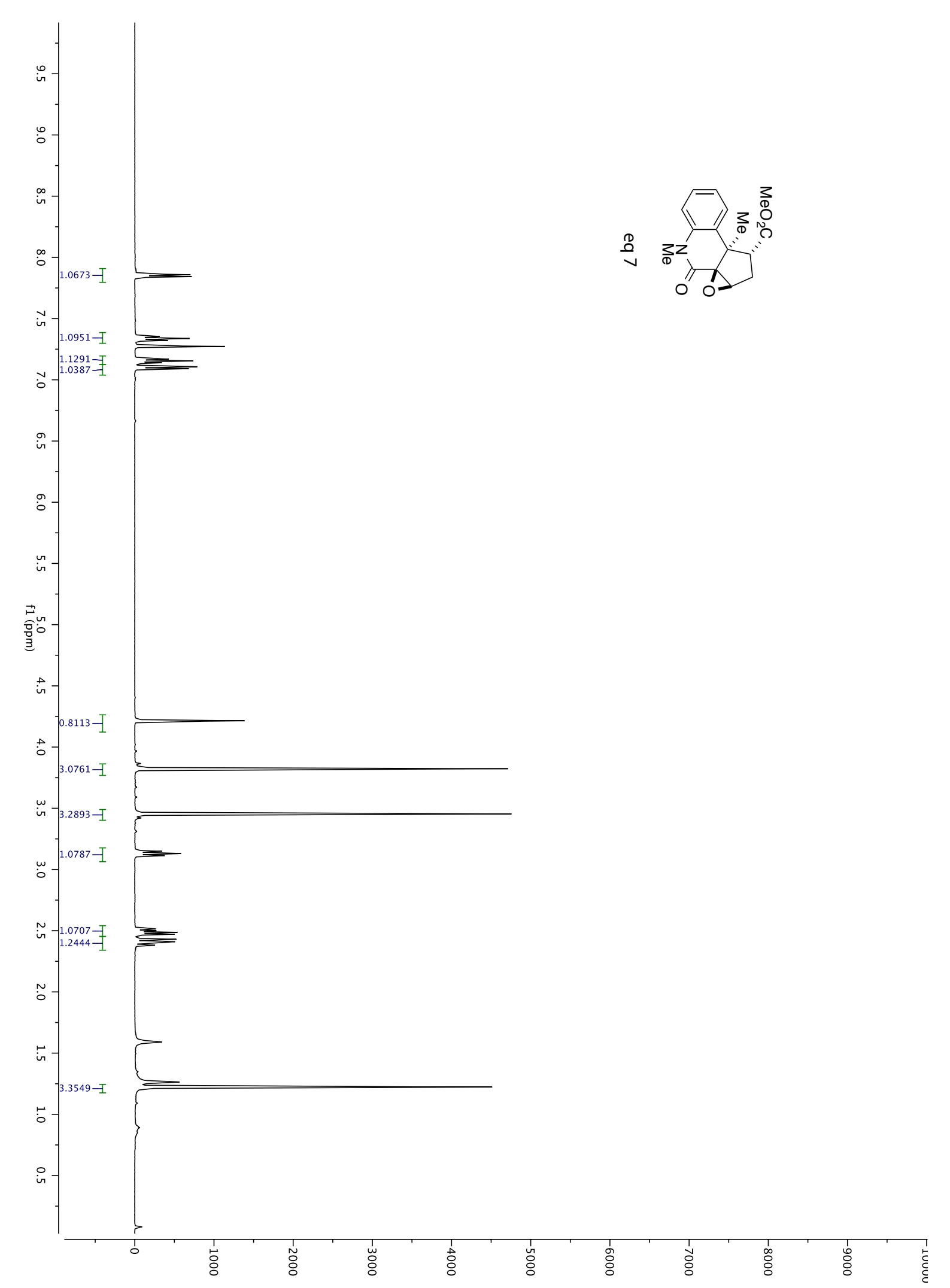

eq 6
H
N
Ts
H
CO2Me
CO2H
f1 (ppm)
2.3286
2.1844
3.1338
1.0000
1.0605
2.0451
3.1600
1.0924
3.2225
1.0674
1.0950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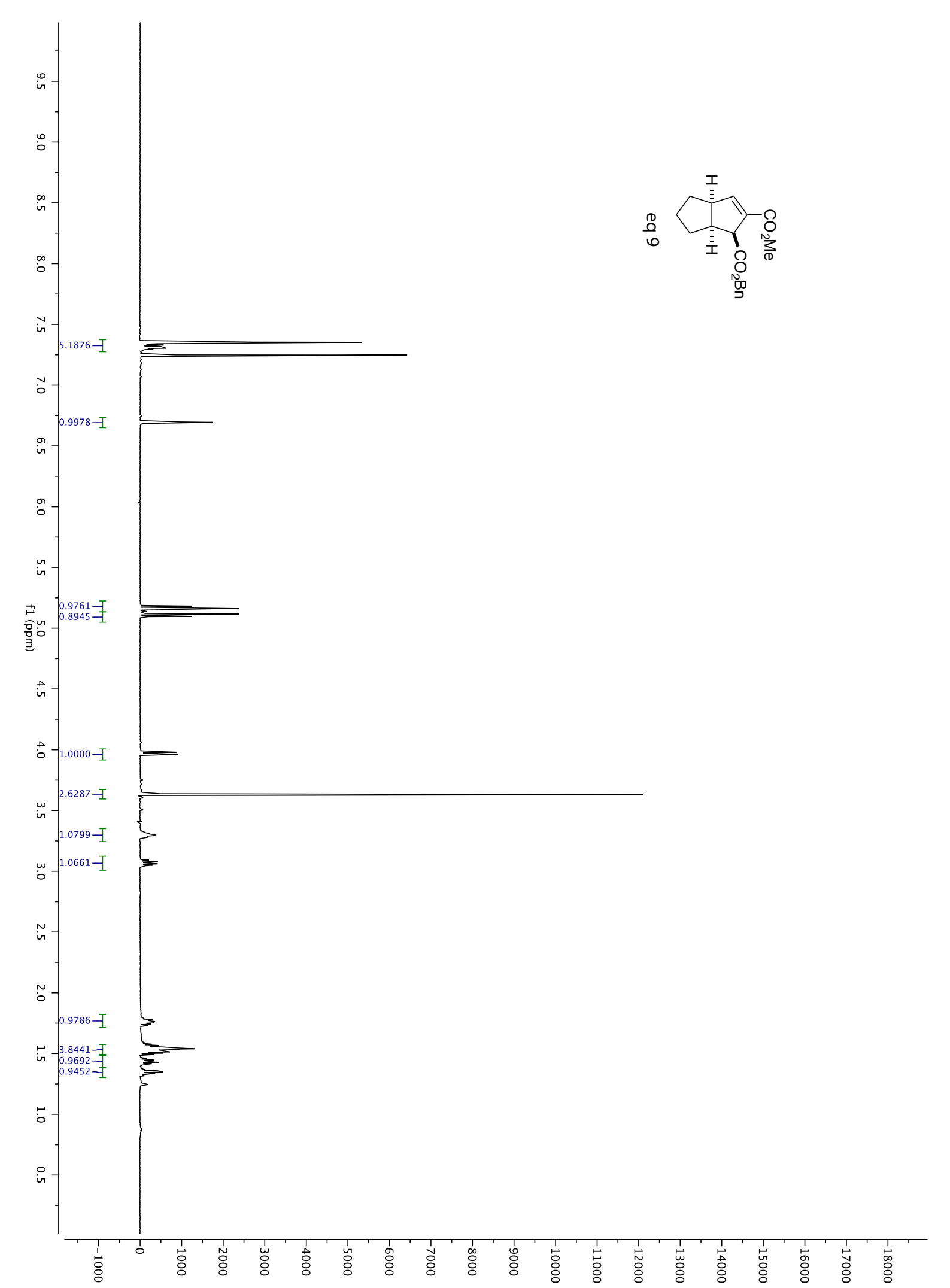
MeO2C
Me
N
Me
O
O
1.0673
1.0951
1.1291
1.0387
0.8113
3.0761
3.2893
1.0787
1.0707
1.2444
3.3549
f1 (ppm)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CO2Me
CO2Bn
H
H
f1 (ppm)
5.1876
0.9978
0.9761
0.8945
1.0000
2.6287
1.0799
1.0661
0.9786
3.8441
0.9692
0.9452